EXHIBIT D

ANALYTICAL METHODS
FOR VOLATILE ORGANIC COMPOUNDS

Exhibit D - Analytical Methods for Volatile Organic Compounds

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1.0 SCOPE AND APPLICATION

1.1 The analytical method that follows is designed to analyze water, sediment, soil, other solid matrices and oily sludges from hazardous waste sites for the organic compounds on the Target Compound List (Exhibit C, VOA TCL). This method is based on EPA Method 624 (Purgeables) and SW-846 Method 5035.

1.1.1 The Target Compound List for this method is equivalent to the VOA TCL and includes the Region I Modified, Method 524.2 Target Compounds (except for bromochloromethane) with elevated CRQLs.

1.1.2 The target compound list may be designated as all compounds listed in Exhibit C VOA TCL or a subset of those compounds and will be indicated on the chain of custody accompanying each sample delivery group (SDG).

1.2 The method includes sample preparation, a hexadecane screening procedure on a GC/FID to determine the approximate concentration of organic constituents in the sample (Appendix A), and the actual analysis which is based on a purge and trap gas chromatograph/mass spectrometer (GC/MS) method.

1.3 The method includes volatile analysis of low level soil samples by a Closed System Purge-and-Trap. Modified SW-846 Method 5035 for Volatiles in Low Level Soils is provided Appendix B.

1.4 Problems have been associated with the following compounds analyzed by this method:

- Chloromethane, vinyl chloride, bromomethane, and chloroethane can display peak broadening if the compounds are not delivered to the GC column in a tight band.
- Acetone, hexanone, 2-butanone, and 4-methyl-2-pentanone have poor purge efficiencies.
- 1,1,1-trichloroethane and all the dichloroethanes can dehydrohalogenate during storage or analysis.
- Chloromethane can be lost if the purge flow is too fast.
- Bromoform is one of the compounds most likely to be adversely affected by cold spots and/or active sites in the transfer lines. Response of its quantitation ion (m/z 173) is directly affected by the tuning of the GC/MS to meet the instrument performance criteria for 4-bromofluorobenzene (BFB) at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve bromoform response.

2.0 SUMMARY OF METHOD

2.1 Water

An inert gas is bubbled through a 5 ml sample contained in a specifically designed purging chamber at ambient temperature. The purgeable compounds are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeable compounds onto a gas chromatographic column. The gas chromatograph is temperature-programmed to separate the purgeable compounds which are then detected with a mass spectrometer.

2.2 Low Soil/Sediment/Solid Samples

An inert gas is bubbled through a mixture of reagent water and 5 g of sample contained in a specifically designed purging chamber that is held at an elevated temperature. The purgeable compounds are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeable compounds onto a gas chromatographic column. The gas chromatograph is temperature-programmed to separate the purgeable compounds which are then detected with a mass spectrometer. Exhibit D Volatiles and Appendix B, Modified SW-846 Method 5035 for Volatiles in Low Level Soils have the specifics for the closed-system purge-and-trap procedures.

2.3 Medium Soil/Sediment/Solid Samples

A measured amount of sample is extracted with methanol. A portion of the methanol extract is diluted to 5 ml with reagent water. An inert gas is bubbled through this solution in a specifically designed purging chamber at ambient temperature. The purgeable compounds are effectively transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeable compounds onto a gas chromatographic column. The gas chromatograph is temperature-programmed to separate the purgeable compounds which are then detected with a mass spectrometer.

2.4 Oily Sludges

A measured amount of sludge is extracted with methanol or, if the sample is methanol soluble, the aliquot is diluted with methanol. A portion of the extract or diluent is diluted to 5 ml with reagent water. An inert gas is bubbled through this solution in a specifically designed purging chamber at ambient temperature. The purgeable compounds are effectively transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeable compounds onto a gas chromatographic column. The gas chromatograph is temperature-programmed to separate the purgeable compounds which are then detected with a mass spectrometer.

2.5 Method Detection Limits

Prior to analysis, method detection limits (MDLs) for all compounds in Exhibit C, VOA TCL, must be established in accordance with 40 Code of Federal Regulations, Part 136, Appendix B. All MDL values must be less than or equal to one-third of the CRQL. The MDL studies must be conducted using the same specifications as for sample analysis. These specifications include but are not limited to: GC/MS instrument performance check technical acceptance criteria, method blank conditions and technical acceptance criteria, initial and continuing calibration conditions and technical acceptance criteria and all instrument operating conditions. The MDL studies must be conducted prior to sample analysis, for each alternate trap/column/technique and/or at least annually, whichever, is more frequent. For aqueous samples, seven aliquots of reagent water are spiked with all TCL VOA at 2 to 5 times

the expected MDLs and are analyzed by ambient purge and trap GC/MS. For solid matrices, seven aliquots of a clean solid matrix (such as sand) are spiked with all TCL VOA at 2 to 5 times the expected MDLs and are analyzed by heated purge and trap GC/MS. All sequential analyses of MDL standards must be reported and used in the resulting MDL values which are calculated. The MDL results are calculated as described in 40 CFR, Part 136, Appendix B and reported as a separate SDG in accordance with Exhibit B. The appropriate Students' t value must be clearly provided with the algorithm used to calculate the MDL values. MDLs shall be determined and reported for each instrument/trap/column and method.

The MDL study must be reported as detailed in Exhibit B. The individual analytical sequence raw data must be provided and these data must be summarized in a table which demonstrates the calculated MDL values. The summarized MDL results table must include the concentration found for each compound in each aliquot, the mean concentration of each compound, the percent recovery of each compound, the standard deviation for each compound, and the Method Detection Limit. The true concentration of the compound in the spike solution must also be provided. The table must list the compounds in the same order as they appear in the target compound list in Exhibit C. In addition, the MDL values for each instrument and method used in reporting results for an SDG shall be submitted with each data package.

The annually determined MDL for an instrument and method shall always be used as the MDL for that instrument/method during that year. If the instrument/method is adjusted in any way that may affect the MDL, the MDL for that instrument/method must be redetermined and the results submitted for use as the established MDL for that instrument/method for the remainder of the year.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks as described in Section 12. The use of non-Polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during storage and handling. Sample storage conditions must be demonstrated to be free from contamination by analyzing and reporting a storage blank with each SDG as described in Section 12.0.

4.3 Contamination by carryover can occur whenever high level and low level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution between analyses, rinse it with distilled water, and then dry it in an oven at 105 °C. The trap and other parts of the system are also subjected to contamination; therefore, frequent bakeout and purging of the entire system may be required.

4.4 The laboratory where volatile analysis is performed should be completely free of solvents.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis.

5.2 The following compounds covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this SOW is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the SDG Narrative.

6.1 Glassware

6.1.1 Syringes - 5 ml, gas-tight with shut-off valve. Micro syringes - 25 µl and larger, 0.006 inch ID needle.

6.1.2 Syringe Valve - two-way, with Luer ends (three each), if applicable to the purging device.

6.1.3 Pasteur Pipets - disposable.

6.1.4 Vials and Caps - 2 ml for GC.

6.1.5 Volumetric Flasks.

6.1.6 Bottle - 15 ml, screw-cap, with Teflon cap liner.

6.2 Miscellaneous Supplies

6.2.1 pH Paper - narrow range

6.2.2 Drying Oven

6.2.3 Dessicator

6.2.4 Crucibles - Porcelain

6.2.5 Aluminum Weighing Pans

6.2.6 Encore™ sampler & supplies (En Chem, Inc.) or equivalent

6.3 Balances - analytical, capable of accurately weighing ± 0.0001 g, and a top-loading balance capable of weighing 100 g ± 0.01 g. The balances must be calibrated in accordance with ASTM E 617 specifications each 12-hour work shift. The balances must also be annually checked by a certified technician.

6.4 Purge and Trap Device - consists of three separate pieces of equipment: the sample purge chamber, trap, and the desorber. Several complete devices are commercially available.

6.4.1 The sample purge chamber must be designed to accept 5 ml samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 ml. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column.

6.4.2 The low soil purge-and-trap system consists of a unit that automatically adds water, surrogates, and internal standards to a vial containing the sample without opening the vial, purges the VOCs using an inert gas stream while agitating the contents of the vial, and also traps the realeased VOCs for subsequent desorption into the gas chromatograph. Such systems are commercially available from several sources and shall meet the following specifications.

6.4.2.1 The purging device should be capable of accepting a vial sufficiently large to contain a 5 gm soil sample plus a magnetic stirring bar and 10 mL of water. The device must be capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 5 mL of organic-free reagent water

into the sample vial while trapping the displace headspace vapors. It must also be capable of agitating the sealed sample during purging, (e.g., using a magnetic stirring bar added to the vial prior to sample collection, sonication, or other means). The analytes being purged must be quantitatively transferred to an adsorber trap. The trap must be capable of transferring the absorbed VOCs to the gas chromatograph.

Note: The equipment used to develop this method was a Dynatech PTA-30 W/S Autosampler. This device was subsequently sold to Varian, and is now available as the Archon Purge and Trap Autosampler. See the disclaimer in Section 6.0 for guidance on the use of alternative equipment.

6.4.3 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch. The trap must be packed to contain the following minimum lengths of adsorbents: (starting from inlet) 0.5 cm silanized glass wool, 1 cm methyl silicone, 15 cm of 2,6-diphenylene oxide polymer (Tenax-GC, 60/80 mesh), 8 cm of silica gel (Davison Chemical, 35/60 mesh, grade 15 or equivalent), 7 cm of cocunut charcoal (prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen), and 0.5 cm silanized glass wool. A description of the trap used for analysis shall be provided in the SDG narrative.

6.4.4 The desorber should be capable of rapidly heating the trap to 180 °C. The polymer section of the trap should not be heated higher than 180 °C and the remaining sections should not exceed 220 °C during bakeout mode.

6.4.5 Trap Packing

6.4.5.1 2,6-Diphenylene oxide polymer, 60/80 mesh chromatographic grade (Tenax GC or equivalent).

6.4.5.2 Methyl silicone packing, 3.0 percent OV-1 on Chromasorb W, 60/80 mesh (or equivalent).

6.4.5.3 Silica gel, 35/60 mesh, Davison, grade 15 (or equivalent).

6.4.5.4 Coconut charcoal (prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen).

6.4.5.5 The Contractor may choose to use alternate sorbent traps. However, the alternate sorbent trap selected must meet all the method technical acceptance criteria established in the SOW and Exhibit E.

- The trap packing materials must not introduce contaminants which interfere with identification and quantitation of the compounds listed in Exhibit C (Volatiles).
- The sorbent trap must be able to accept up to the high point calibration standard without becoming overloaded.
- The alternate sorbent trap must be used for the entire analysis; including the MDL study, initial and continuing calibration, and all blank, QC sample and sample analyses. If a new alternate sorbent trap is chosen after the initial MDL study has been completed, then the MDL study must be reanalyzed using that alternate column. Analytical results generated using any alternate trap must meet all technical acceptance criteria listed in the SOW and the CRQLs listed in Exhibit C (Volatiles).

6.4.5.5.1 The alternate trap must be designed to optimize performance. Follow manufacturer's instructions for the use of its product. Before use of any trap, other than the one specified in 6.4.2, the Contractor must meet the criteria listed in 6.4.4.4. Other sorbent traps include, but are not limited to, Tenax/Silica Gel/Carbon Trap from EPA Method 524.2, Tenax-GC/Graphpac-D Trap (Alltech) or equivalent, and Vocarb 4000 Trap (Supelco) or equivalent. The Contractor must

document the trap composition (packing material/brand name, amount of packing material) in each SDG Narrative.

6.4.5.5.2 Manufacturer provided technical information concerning the performance characteristics of the sorbent trap must be included in the MDL Study data package to support the use of the alternate sorbent trap.

6.4.6 The purge and trap apparatus may be assembled as a separate unit or be an integral unit coupled with a gas chromatograph.

6.5 A heater capable of maintaining the purge chamber at 40 °C ± 1 °C must be used for low level soil/sediment analysis, but not for water, medium level soil/sediment or oily sludge analyses.

6.6 Gas Chromatograph/Mass Spectrometer (GC/MS) System

6.6.1 Gas Chromatograph - the gas chromatograph (GC) system must be capable of temperature programming and must maintain an optimal flow rate throughout trap desorption and GC temperature program operations. The system must include or be interfaced to a purge and trap system as specified in Section 6.4 and have all required accessories including syringes, GC columns, and gases.

6.6.2 Gas Chromatography Columns

A description of the GC column used for analysis shall be provided in the SDG Narrative.

6.6.2.1 Packed columns **must not** be used. Capillary columns **must** be used to achieve the required separation of all isomers listed in the VOA TCL provided in Exhibit C (Volatiles).

6.6.2.2 Capillary Columns

6.6.2.2.1 Minimum length 30 m x 0.53 mm ID VOCOL (Supelco) or equivalent fused silica widebore capillary column with 3 μm film thickness.

6.6.2.2.2 Minimum length 30 m x 0.53 mm ID DB-624 (J & W Scientific) or equivalent fused silica widebore capillary column with 3 μm film thickness.

6.6.2.2.3 Minimum length 30 m x 0.53 mm ID AT-624 (Alltech) or equivalent fused silica widebore capillary column with 3 μm film thickness.

6.6.2.2.4 Minimum length 30 m x 0.53 mm ID HP-624 (Hewlett-Packard) or equivalent fused silica widebore capillary column with 3 μm film thickness.

6.6.2.2.5 Minimum length 30 m x 0.53 mm ID RTx-624 (Restek) or equivalent fused silica widebore capillary column with 3 μm film thickness.

6.6.2.2.6 Minimum length 30 m x 0.53 mm ID BPX-624 (SGE) or equivalent fused silica widebore capillary column with 3 μm film thickness.

6.6.2.2.7 Minimum length 30 m x 0.53 mm ID CP-Sil 13CB (Chrompack) or equivalent fused silica widebore capillary column with 3 μm film thickness.

6.6.3 The Contractor may choose to use an alternate capillary column. However, the alternate capillary column selected must meet all the method technical acceptance criteria established in the SOW and Exhibit E.

- The GC column must not introduce contaminants which interfere with identification and quantitation of the compounds listed in Exhibit C (Volatiles).

- The GC column must be able to accept concentrations up to the high point standard of each target compound without becoming overloaded.
- The GC column must provide equal or better resolution of the target compounds than the columns listed above.
- The alternate GC column must be used for the entire analysis, including the MDL study, initial and continuing calibration, and all blank, QC sample and all sample analyses. If a new alternate GC column is chosen after the initial MDL study has been completed, then the MDL study must be reanalyzed using that alternate column. Analytical results generated using any alternate trap must meet all technical acceptance criteria listed in the SOW and the CRQLs listed in Exhibit C (Volatiles).

6.6.3.1 The alternate GC column must be designed to optimize performance. Follow manufacturer's instructions for the use of its product. Before use of any column, other than the ones specified in 6.6.2.2, the Contractor must meet the criteria listed in 6.6.3. Once this has been demonstrated, the Contractor must document the column used (brand name, length, diameter, and film thickness) in each SDG Narrative.

6.6.3.2 Manufacturer provided technical information concerning the performance characteristics of the GC column must be included in the MDL Study data package to support the use of the alternate column.

6.6.4 The carrier gas for routine GC/MS applications is helium. The purge gas can be either helium or nitrogen. High purity gases must be used to ensure a contaminant free GC/MS system. All carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with rubber components are not to be used.

6.6.5 Mass Spectrometer - must be capable of scanning from 35 to 300 amu every 1 second or less utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the instrument performance acceptance criteria when 50 ng of BFB is injected through the gas chromatograph inlet. The instrument conditions required for the acquisition of the BFB mass spectrum are given in Section 9.0. The MS must have the capability to be tuned using manufacturers specifications for perfluoro-tri-n-butylamine.

6.6.5.1 The MS scan rate should allow acquisition of at least five spectra while a sample compound elutes from the GC. The purge and trap GC/MS system must be in a room whose atmosphere is demonstrated to be free of all potential contaminants which will interfere with the analysis. The instrument must be vented to the outside of the facility or to a trapping system which prevents the release of contaminants into the instrument room.

6.6.6 GC/MS interface - any gas chromatograph to mass spectrometer interface that produces the data which meet the technical acceptance criteria established in the SOW and Exhibit E. Gas chromatograph to mass spectrometer interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

6.6.7 Data system - a computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage, on machine-readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against

reference library spectra. The NIST/EPA/NIH (May 1992 release or most recent release) and/or Wiley (1991 release or most recent elease), or equivalent mass spectral library shall be used as the reference library. The most recent release of the reference library must be utilized. The data system must be capable of flagging all data files that have been edited manually by laboratory personnel since every manual edit must be flagged on the quantitation reports.

6.6.8 Magnetic tape storage device - must be capable of recording data and must be suitable for long-term, off-line storage.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent water - defined as water in which no interferant, target or non-target compound is observed at or above the CRQL of the compounds of interest. Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g (1 lb) of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

7.1.1.1 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

7.1.1.2 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

7.1.2 Methanol - pesticide quality or equivalent

7.1.3 Dow Corning anti-foaming agent 1510 emulsion 10% active, approximately one drop per 5 mls of sample, or equivalent.

7.2 Standards

7.2.1 Standards Documentation

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure described in Exhibit E. The Contractor must be able to verify that the standards are certified by producing the manufacturer's certificates and/or generating the documentation as described in Exhibit E. Manufacturer's certificates of analysis must be retained by the Contractor for the term of the contract. The documentation may be requested during an on-site audit.

7.2.2 Stock Standard Solutions

7.2.2.1 Stock standard solutions may be purchased or may be prepared in methanol from pure reference materials.

7.2.2.2 Prepare stock standard solutions by placing about 9.8 ml of methanol into a 10 ml ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes, or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.2.2.3 Add the assayed reference material as described below.

7.2.2.3.1 If the compound is a liquid, using a 100 µl syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

7.2.2.3.2 If the compound is a gas at room temperature, fill a 5 ml valved gas-tight syringe with the reference standard to the 5 ml mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The gas will rapidly dissolve in the methanol.

7.2.2.3.3 The procedure in Section 7.2.2.3.2 may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of the reference standard into the methanol meniscus.

7.2.2.3.4 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. For non-gaseous compounds, calculate the concentration in micrograms per microliter from the net gain in weight. When compound purity is assayed to be 97.0 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard. If the compound

purity is assayed to be less than 97.0 percent, the weight must be corrected when calculating the concentration of the stock solution. (See Exhibit E Analytical Standards Requirements). For gaseous compounds, calculate the concentration in micrograms per microliter, using the Ideal Gas Law, taking into account the temperature and pressure conditions within the laboratory.

7.2.2.3.5 Prepare fresh stock standards every two months for gases or for reactive compounds such as styrene. All other stock standards for non-gaseous/non-reactive purgeable compounds must be replaced six months after the preparation date (or the date opened for purchased stock standards). The stock standards must be replaced sooner if the standard has demonstrated signs of degradation or evaporation.

7.2.3 Secondary Dilution Standards

7.2.3.1 Using stock standard solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. Secondary dilution standard solutions should be prepared at concentrations that can be easily diluted to prepare working standard solutions.

7.2.3.2 Prepare fresh secondary dilution standards for gases and for reactive compounds such as styrene every month, or sooner, if standard has degraded or evaporated. Secondary dilution standards for the other purgeable compounds must be replaced six months after the preparation date (or the date opened for purchased standards). The standards must be replaced sooner if the standard has demonstrated signs of degradation or evaporation.

7.2.4 Working Standards

7.2.4.1 System Monitoring Compound (SMC) Spiking Solution

Prepare a system monitoring compound spiking solution containing 1,2-Dichloroethane-d4 and 1,2-Dichlorobenzene-d4 in methanol at a concentration of 25 µg/ml. Add 10 µl of this spiking solution into 5 ml of sample, sample extract, blank, QC sample or ICV calibration standard for a concentration of 50 µg/L. Prepare fresh spiking solution weekly, or sooner if the solution has degraded or evaporated.

7.2.4.2 Matrix Spiking Solution

Prepare a matrix spiking solution in methanol that contains the following compounds at a concentration of 25 µg/ml: Vinyl chloride, Trichloroethene, 1,2-Dichloroethane, Carbon tetrachloride, Benzene, 1,2-Dichloropropane, Bromoform, 1,1,2-Trichloroethane, cis-1,3-Dichloropropene, Tetrachloroethene, 1,2-Dibromoethane, 2-Hexanone, Tetrahydrofuran and 1,4-Dichlorobenzene. Matrix spike/matrix spike duplicate samples are prepared and analyzed as described in Section 12.2 at a concentration of 50 µg/L. Prepare fresh spiking solution every month, or sooner if the solution has degraded or evaporated.

7.2.4.3 Internal Standard Spiking Solution

Prepare an internal standard spiking solution containing fluorobenzene and chlorobenzene-d5 in methanol at a concentration of 25 µg/mL for each internal standard. Add 10 µL of this internal standard spiking solution into 5 mL of sample, sample extract, blank, QC sample or calibration standard for a concentration of 50 µg/L. Prepare fresh spiking solution weekly, or sooner if the solution has degraded or evaporated.

7.2.4.4 Instrument Performance Check Solution - 4-Bromofluorobenzene (BFB)

Prepare either a 25 ng/µL or 50 ng/µL solution of BFB in methanol. Introduce 50 ng of BFB into the GC either by purging a spiked 5 ml aliquot of reagent water or by direct injection. Prepare fresh

BFB solution weekly, or sooner if the solution has degraded or evaporated.

7.2.4.5 Calibration Standard Solution

Prepare a calibration standard solution containing all of the purgeable target compounds in methanol. The recommended concentration of the target compounds is 100 µg/mL. Tetrahydrofuran and 1,4-dioxane have higher CRQLs and should be prepared at 2 and 5 times greater levels, respectively, than the other target compounds. Up to two separate standard mixes may be prepared by the contractor but all standards must meet acceptance criteria set forth by the SOW. Prepare fresh calibration standard solutions weekly, or sooner if solutions have degraded or evaporated.

7.2.4.6 Initial Calibration Verification Standard Solution

Prepare an initial calibration verification standard solution of all the purgeable target compounds in methanol at the same concentration specified for the Calibration Standard Solution described in Section 7.2.4.5. The standard must be prepared from a source/supplier other than the source of the intial calibration standards. Prepare fresh an initial calibration verification standard solution each time an initial calibration is prepared and analyzed.

7.2.4.7 Initial Calibration, Initial Calibration Verification and Continuing Calibration Standards

7.2.4.7.1 Initial Calibration Standards - Prepare five aqueous initial calibration standard solutions containing all of the purgeable target compounds and system monitoring compounds, except 1,4-dioxane and tetrahydrofuran, at 10, 20, 50, 100, 200 µg/L levels. The concentrations of tetrahydrofuran and 1,4-dioxane in the intial calibration curve should be 2 and 5 times greater, respectively, than the other target compounds. It is required that all three xylene isomers (o-, m-, and p-xylene) be present in the calibration standards at concentrations of each isomer equal to that of the other target compounds (i.e., 10, 20, 50, 100 and 200 µg/L). Similarly, the cis and trans isomers of 1,2-dichloroethene must both be present in the standards at concentrations of each isomer equal to that of the other target compounds.

7.2.4.7.2 Initial Calibration Verification Standard - Prepare an aqueous initial calibration verification standard (Section 7.2.4.6), containing all of the purgeable target compounds and system monitoring compounds at the midpoint level of the calibration curve (50 µg/L for all target compounds; except for tetrahydrofuran at 100 µg/L and 1,4-dioxane at 250 µg/L).

7.2.4.7.3 Continuing Calibration Standard - The midpoint calibration standard is the continuing calibration standard. The concentration of the continuing calibration standard must be at 50 µg/L for all target compounds; except for tetrahydrofuran at 100 µg/L and 1,4-dioxane at 250 µg/L.

7.2.4.7.4 Aqueous calibration standards may be prepared in a volumetric flask or in the syringe used to inject the standard into the purging device.

7.2.4.7.4.1 Volumetric flask - add an appropriate volume of the 100 µg/mL calibration standard solution (Section 7.2.4.5) to an aliquot of reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcohol standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Bring to volume. Mix by inverting the flask three times only. Discard the contents contained in the head of the flask.

7.2.4.7.4.2 Syringe - remove the plunger from a 5 mL "Luerlock" syringe. Pour reagent water into the syringe barrel to just short of

overflowing. Replace the syringe plunger and compress the water. Invert the syringe, open the syringe valve and vent any residual air. Adjust the water volume to 5 mL minus the amount of calibration standard to be added. Withdraw the plunger slightly and add an appropriate volume of working calibration standard solution (Section 7.2.4.5) through the valve bore of the syringe. Close the valve and invert three times.

7.2.4.7.4.3 The methanol contained in each of the aqueous calibration standards must not exceed 1.0 percent by volume.

7.2.5 Ampulated Standard Extracts

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained for 2 years from the manufacturer's preparation date, unless the manufacturer recommends a shorter time period. Standard solutions prepared by the Contractor which are immediately ampulated in glass vials may be retained for 2 years from the Contractor's preparation date. Upon breaking the glass seal, the expiration times listed in Sections 7.2.2 through 7.3 will apply. The Contractor is responsible for assuring that the integrity of the standards has not degraded by following proper storage procedures (see Section 7.3).

7.3 Storage of Standard Solutions

7.3.1 Store the stock standards in Teflon-sealed screw-cap bottles with zero headspace at -10 °C to -20 °C, and protect the standards from light.

7.3.2 Store secondary dilution standards in Teflon-sealed screw-cap bottles with minimal headspace at -10 °C to -20 °C, and protect the standards from light. The secondary dilution standards must be checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

7.3.3 Aqueous working standards may be stored for up to 24 hours if held in Teflon-sealed screw-cap vials with zero headspace at 4 °C (±2 °C). Protect the standards from light. If not so stored, they must be discarded after one hour unless they are set up to be purged by an autosampler. When using an autosampler, the standards may be kept for up to 12 hours in purge tubes connected via the autosampler to the purge and trap device.

7.3.4 Purgeable standards must be stored separately from other standards.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Sample Collection and Preservation

8.1.1 Water samples must be collected in glass containers having a total volume of at least 40 ml with a Teflon-lined septum and an open top screw-cap.

The soil sample containers required will depend on the purge-and-trap system to be employed and the level of analysis. Soil samples may be collected in preweighed glass containers, or Encore™ samplers or equivalent.

8.1.2 For samples received in containers other than glass, the Contractor shall contact the RSCC to ascertain the proper procedure for subsampling from the sample container.

8.1.3 For collection of water samples, the container must be filled by the sampler in such a manner that no air bubbles pass through the sample as the container is being filled. The vial is sealed by the sampler so that no air bubbles are entrapped in it. Two vials are filled and submitted for analysis.

8.1.3.1 If one water sample vial has an air bubble and the other does not, then use the other vial for analysis.

8.1.3.2 If both vials have air bubbles, then analyze the sample vial which has fewer and/or smaller air bubbles.

8.1.3.3 If both vials have air bubbles greater than pea-size, then the Contractor shall contact the RSCC to ascertain whether or not the sample should be analyzed.

8.1.3.4 For all samples that contain air bubbles, regardless of size, the Contractor shall note the problem, the EPA sample number, the EPA sample tag number for the affected samples and any regional instructions in the SDG Narrative.

8.1.4 Water samples are preserved to a pH of 2 at the time of collection. Water samples not amenable to preservation with acid will not be acidified by the sampler. This fact will be noted on the chain of custody form included with the sample shipment. These unpreserved samples must be analyzed within four days of validated time of sample receipt.

8.1.5 Soil samples will be submitted in either Encore™ samplers or vials. If Encore™ samplers are provided the shipment will consist of three samplers and one vial. The three samplers are for volatile analysis and the vial is for percent moisture determination. The three samplers must be prepared, two samplers are for aqueous/sodium bisulfate preservation, one sampler is for methanol preservation and the vial is for percent moisture determination. If samples are provided in vials, two vials will be aqueous/sodium bisulfate preserved, one vial will have methanol preservation and the fourth will be for percent moisture determination.

8.1.6 For soil samples collected in Encore™ samplers the samples must be transferred to glass vials within 48 hrs of sample collection. See Appendix B, Section 9.3 Sample Preparation.

8.1.6.1 Low soil sample preparation is provided in Appendix B, Section 9.3. Low soil samples are preserved with sodium bisulfate.

8.1.6.2 Medium soil samples are placed in the preweighed sample vial with 10 mL of methanol. The sample vial, with 10 mL of methanol and all labeling, is weighed to the nearest 0.1 g prior to the addition of sample.

8.1.7 All soil samples must be weighed to the nearest 0.1 gm prior to sample analysis. All descrepancies, differences between the laboratory weight and the field weight, must immediately be reported to the Regional Sample Control Coordinator.

8.1.8 All samples must be iced or refrigerated at 4 °C (±2 °C) from the time of collection until analysis.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4 °C (±2 °C) from the time of receipt until 60 days after delivery of a reconciled, complete sample data package to the Agency. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 If sample storage temperatures exceed 4°C (±2 °C) and/or samples are not light protected, then the Contractor shall contact the RSCC to ascertain whether or not the samples should be analyzed. For all samples that were not properly refrigerated and/or light protected, the Contractor shall note the problem, the EPA sample numbers for the affected samples, and the Regional instructions in the SDG Narrative.

8.2.3 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants and in a refrigerator used only for storage of volatile samples.

8.2.4 All volatile samples in an SDG must be stored together in the same refrigerator.

8.2.5 Storage blanks shall be stored with the samples contained in an SDG until all samples are analyzed. The storage blank shall be analyzed concurrently with the last sample in the SDG and the results shall be included in the data package per the reporting requirements contained in Exhibit B.

8.2.6 Samples, sample extracts and standards must be stored separately.

8.2.7 Volatile standards must be stored separately from semivolatile and pesticide/Aroclor standards.

8.3 Contract Required Holding Times

8.3.1 Analysis of water, soil/sediment/solid and oily sludge samples must be completed within ten (10) days of Validated Time of Sample Receipt (VTSR). Unpreserved water samples must be analyzed within four (4) days of VTSR. As part of the Agency's QA program, the Agency may provide Performance Evaluation (PE) samples which the Contractor is required to prepare per the instructions provided by the Agency. The PE samples must be analyzed and reported with the SDG with which they were submitted.

8.3.2 All soil samples collected in Encore™ samplers or equivalent must be transferred to vials within 48 hrs of sample collection see Appendix B, Section 9.3 Sample Preparation. The time and date of sample transfer must be recorded in a laboratory logbook and provided with the data package. A visual description including the sample color, approximate particle size and/or sample consistency must be recorded in a laboratory logbook and provided with the data package.

8.3.3 All low level soil samples must be weighed at the laboratory prior to analysis. All discrepancies must be immediately reported to the Regional Sample Control Coordinator.

If medium level soil samples are prepared in the field, received at the laboratory as 5 gms of soil samples in 10 mL methanol, the samples must be weighed at the laboratory before sample analysis. A 1 mL aliquot must be transferred within 48 hrs of receipt to a GC vial and stored until analysis. All discrepancies must be immediately reported to the Regional Sample Control Coordinator.

8.3.4 If samples submitted for volatile analysis have exceeded holding times and have not yet been analyzed, then the Contractor shall contact the RSCC to ascertain whether or not the samples should be analyzed. Note that this notification requirement in no way obviates the contractual requirement for the Contractor to analyze samples within holding times. If the Contractor is instructed to proceed

with analysis outside holding times, sample price may be reduced depending upon the impact of the non-compliance on data usability. For all samples that exceeded holding times, the Contractor shall note the problem, the EPA sample numbers for the affected samples, and the Regional instructions in the SDG narrative.

8.3.5 VOC data reported from sample analyses which were performed outside the contract required holding times for VOC analysis shall be subject to a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Conditions

9.1.1 Purge and Trap - Aqueous

9.1.1.1 The following are the recommended purge and trap analytical conditions.

Purge Conditions

Purge Gas:	Helium or Nitrogen
Purge Time:	11.0 ± 0.1 minute
Purge Flow Rate:	25-40 ml/minute
Purge Temperature:	Ambient temperature for water medium level soil/sediment samples (required); 40 °C low level soil/sediment or oily sludge samples (required)

Desorb Conditions

Desorb Temperature:	180 °C
Desorb Flow Rate:	15 ml/minute
Desorb Time:	4.0 ± 0.1 minute

Trap Reconditioning Conditions

Reconditioning Temperature:	180 °C
Reconditioning Time:	7.0 ± 0.1 minute (minimum). A longer time may be required to bake contamination or water from the system.

9.1.1.2 Before initial use, condition the trap overnight at 180 °C by back flushing with at least 20 ml/minute flow of inert gas. Do not vent the trap effluent onto the analytical column. Prior to daily use, condition the trap by heating at 180 °C for 10 minutes while backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to the analysis of samples.

9.1.1.3 Optimize purge and trap conditions for sensitivity and to minimize cross-contamination between samples. Once optimized, the same purge and trap conditions must be used for the analysis of all standards, samples, QC samples and blanks.

9.1.1.4 A moisture reduction/water management system may be used to improve the chromatographic performance by controlling moisture or water. However, the system must meet all method acceptance criteria established in the SOW and Exhibit E.

- The system must not introduce contaminants which interfere with identification and quantitation of compounds listed in Exhibit C (Volatiles),
- The moisture reduction/water management system must be used for all analyses including the MDL study, initial and continuing calibration, all blank, QC sample and sample analyses. The technical acceptance criteria established in the SOW and Exhibit E must be achieved for these parameters.

9.1.2 Purge and Trap - Soil

9.1.2.1 The soil purge and trap conditions are specified in Appendix B, Section 8.0 Calibration and Standardization.

9.1.3 Gas Chromatograph

9.1.3.1 The following are recommended GC analytical conditions.

Packed columns Must not be used for this methodology

Capillary Columns

Carrier Gas:	Helium
Flow Rate:	2-6 ml/minute (column dependent)
Initial Temperature:	35 °C
Initial Hold Time:	3 - 5 (± 0.1) minutes
Ramp Rate:	8 C°/minute
Final Temperature:	200 °C
Final Hold Time:	15 minutes or until three minutes after all compounds listed in Exhibit C (Volatiles) elute (required).

9.1.3.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, samples and QC samples.

9.1.3.3 For capillary columns, if the gaseous compounds chloromethane, bromomethane, vinyl chloride, and chloroethane fail to exhibit narrow, symmetrical peak shape, are not separated from the solvent front, or are not resolved greater than 90.0 percent from each other, then a subambient oven controller must be used, and the initial temperature must be less than or equal to 10 °C.

9.1.4 Mass Spectrometer

The following are the required mass spectrometer analytical conditions:

Electron Energy:	70 volts (nominal)
Mass Range:	35-300 amu
Scan Time:	To give at least 5 scans per peak, not to exceed 2 seconds per scan for capillary column.

9.1.5 Standard/Sample Analysis

9.1.5.1 Purge and Trap Set Up

9.1.5.1.1 Assemble a purge and trap device that meets the specifications in Section 6.4. Set up and condition the device as described in Section 9.1.1.

9.1.5.1.2 Connect the purge and trap device to the gas chromatograph. The gas chromatograph must be operated using temperature and flow rate parameters equivalent to those established in Section 9.1.2.

9.1.5.1.3 Adjust the purge gas (helium) flow rate to 25-40 ml/minute. Variations from this flow rate may be necessary to achieve better purging and collection efficiencies for some compounds, particularly chloromethane and bromoform.

9.1.5.2 Sample Introduction and Purging

9.1.5.2.1 Remove the plunger from a 5 ml syringe and attach a closed syringe valve. Open the aqueous sample or standard bottle which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5 ml. This process of taking an aliquot destroys the validity of the aqueous sample for future analysis so, if there is only one VOA vial, the analyst must

fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time as the analyst has determined that the first sample has been analyzed properly. Filling one 5 ml syringe would allow the use of only one syringe. If an analysis is needed from the second 5 ml syringe, it must be performed within 24 hours. Care must also be taken to prevent air from leaking into the syringe. Soil/sediment or oily sludge matrices are prepared similarly as described in Sections 10.1.4, 10.1.5 or 10.1.6, respectively.

9.1.5.2.2 Add 10 µl of the system monitoring compound spiking solution (Section 7.2.4.1) and 10 µl of the internal standard spiking solution (Section 7.2.4.3) through the valve bore of the syringe, then close the valve. NOTE: The system monitoring compound and internal standard compound solutions are not added to the GC/MS instrument performance check solution and only the internal standard solution is added to the initial calibration standards. The system monitoring compounds and internal standards may be mixed and added as a single spiking solution. The addition of 10 µl of the system monitoring compound and 10 µl of internal standard spiking solution to 5 ml of sample is equivalent to a concentration of 50 µg/L of each system monitoring compound and internal standard.

9.1.5.2.3 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

9.1.5.2.4 Close both valves and purge the sample for 11.0 ± 0.1 minutes at ambient temperature.

9.1.5.3 Sample Desorption

9.1.5.3.1 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180 °C while backflushing the trap with an inert gas between 20 and 60 ml/minute for four minutes.

9.1.5.3.2 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 ml flushes of reagent water to avoid carryover of target compounds. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution between analyses, rinse it with distilled water, and then dry it in an oven at 105°C.

9.1.5.4 Trap Reconditioning

9.1.5.4.1 After desorbing the sample for four minutes, recondition the trap by returning the purge and trap device to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180 °C. Trap temperatures up to 220 °C may be employed. However, the higher temperature will shorten the useful life of the trap. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

9.2 GC/MS Instrument Performance Check (Tuning) and Ion Abundance

9.2.1 Summary of GC/MS Instrument Performance Check

9.2.1.1 The Mass Spectrometer must be initially tuned to meet the manufacturer's specifications, using a suitable calibrant such as perfluoro-tri-n-butylamine (PFTBA) or perfluorokerosene (PFK).

9.2.1.2 The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (Section 7.2.4.4). Prior to the analysis of any samples, including QC samples, blanks, or calibration standards, the Contractor must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing BFB.

9.2.1.3 If the technical acceptance criteria for GC/MS Instrument Performance Checks are not met, then the contractor must stop and correct the problem before continuing the analytical sequence.

9.2.2 Frequency of GC/MS Instrument Performance Check

The instrument performance check solution must be analyzed once at the beginning of each 12-hour period, during which samples or standards are to be analyzed. The twelve (12) hour time period for GC/MS instrument performance check (BFB), standards calibration (initial or continuing calibration criteria), blank, QC sample and sample analysis begins at the moment of analysis of the BFB analysis that the laboratory submits as documentation of a compliant GC/MS instrument performance check. The time period ends after twelve (12) hours have elapsed according to the system clock.

9.2.3 Procedure for GC/MS Instrument Performance Check

9.2.3.1 The analysis of the GC/MS instrument performance check solution may be performed as follows:

- As an injection of 50 ng of BFB solution into the GC/MS as per Section 7.2.4.4.
- By adding 50 ng of BFB solution to 5 mL of reagent water and analyzing the resulting solution as an environmental sample (see Section 9.1.4). NOTE: Internal standard or system monitoring compound solutions are not added to the BFB analysis.

9.2.3.2 The GC/MS instrument performance check solution must be analyzed alone without calibration standards. BFB key ion abundances are compared to established ion abundance criteria for BFB outlined in Table 1.

9.2.4 Technical Acceptance Criteria for GC/MS Instrument Performance Check

9.2.4.1 The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not background subtract part of the BFB peak.

9.2.4.2 The analysis of the GC/MS instrument performance check solution must meet the ion abundance criteria given in Table 1.

9.2.4.3 All subsequent standards, samples, QC samples, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

9.2.5 Corrective Action for GC/MS Instrument Performance Check

9.2.5.1 If the BFB technical acceptance criteria are not met, retune the GC/MS system (Section 9.2.1). If the GC/MS system cannot be retuned, then it may also be necessary to clean the ion source or take other corrective actions to achieve the GC/MS Instrument Performance check technical acceptance criteria.

9.2.5.2 BFB technical acceptance criteria **must** be met before any standards, samples, including QC samples or required blanks are analyzed. Any samples, QC samples or required blanks analyzed when GC/MS Instrument Performance check technical acceptance criteria have not been met will require reanalysis at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all technical acceptance criteria.

9.2.5.3 Sample analyses reported with a non-compliant GC/MS Instrument Performance Check shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data useability.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

9.3.1.1 Prior to the analysis of samples, QC samples, required blanks, and after the GC/MS instrument performance check solution criteria have been met, each GC/MS system must be calibrated at five concentrations to determine instrument sensitivity and the linearity of GC/MS response for the purgeable target compounds.

9.3.1.2 If the technical acceptance criteria for initial calibration are not met, then the Contractor must stop and correct the problem before continuing the analytical sequence.

9.3.2 Frequency of Initial Calibration

9.3.2.1 Each GC/MS system must be calibrated upon award of the contract, whenever the Contractor takes corrective action which may change or affect the initial calibration criteria (e.g., ion source cleaning or repair, column replacement, etc.), or if the continuing calibration technical acceptance criteria have not been met.

9.3.2.2 If time remains in the 12-hour time period after meeting the technical acceptance criteria for the GC/MS instrument performance check and initial calibration, samples may be analyzed. It is not necessary to analyze a continuing calibration standard if the initial calibration standard that is the same concentration as the continuing calibration standard meets the continuing calibration technical acceptance criteria. A method blank is required. Quantify all sample and quality control sample results, such as internal standard area response change and retention time shift,

against the initial calibration standard that is the same concentration as the continuing calibration standard.

9.3.3 Procedure for Initial Calibration

9.3.3.1 Add 10 µl of the internal standard solution (Section 7.2.4.3) to each of the five aqueous calibration standard solutions prepared as described in section 7.2.4.7.1. The system monitoring compounds are included in the calibration standard solutions. Analyze each calibration standard according to Section 9.1.4.

9.3.3.2 Separate initial and continuing calibrations must be performed for water samples and low soil samples. Extracts of medium level soil/sediment or oily sludge samples may be analyzed using the calibrations for water samples.

9.3.4 Calculations for Initial Calibration

9.3.4.1 Calculate the relative response factor (RRF) for each volatile target and system monitoring compound using Equation 1. The primary characteristic ions used for quantitation of target compounds, system monitoring compounds and internal standards are listed in Table 2 and Table 4. Assign each target compound, and system monitoring compound to an internal standard according to Table 3. If an interference prevents the use of a primary ion for a given target compound or internal standard, use a secondary ion listed in Table 2 or 4. NOTE: Unless otherwise stated, the area response of the primary characteristic ion is the quantitation ion. If a secondary ion is used for quantitation in a sample the initial and continuing calibration standards must also be calculated using the secondary ion.

EQ. 1

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where,

A_x = Area of the characteristic ion (EICP) for the compound to be measured (see Table 2)
A_{is} = Area of the characteristic ion (EICP) for the specific internal standard (see Tables 3 and 4)
C_{is} = Concentration of the internal standard
C_x = Concentration of the compound to be measured

9.3.4.2 Calculating the relative response factor (RRF) of the xylenes requires special attention. On capillary columns, the m-xylene and p-xylene isomers coelute. Therefore, quantitation of total xylenes shall be based on the RRF for o-xylene which does not coelute.

9.3.4.3 All other isomeric compounds such as cis/trans-1,2-dichloroethene and the dichlorobenzenes must be resolved chromatographically and reported as separate compounds with unique RRFs.

9.3.4.4 The mean relative response factor ($\overline{RRF}$) must be calculated for all compounds using Equation 2.

EQ. 2

$$\overline{RRF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where,

$\overline{RRF}$ = the mean of n values,
RF_i = each individual value used to calculate the mean,
n = the total number of values.

9.3.4.5 Calculate the % Relative Standard Deviation (%RSD) of the RRF values over the working range of the curve using Equation 3.

EQ. 3

$$\%RSD = \frac{Standard\ Deviation}{\overline{RRF}} \times 100$$

Where,

$$Standard\ Deviation = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RRF})^2}{(n-1)}}$$

9.3.5 Technical Acceptance Criteria for Initial Calibration

9.3.5.1 All initial calibration standards must be analyzed at the concentration levels described in Section 7.2.4.7.1, and at the frequency described in Section 9.3.2 on a GC/MS system meeting the GC/MS Instrument Performance Check technical acceptance criteria.

9.3.5.2 The relative response factor (RRF) at each calibration concentration for each purgeable target and system monitoring compound must be greater than or equal to the compound's minimum acceptable response factor listed in Table 5.

9.3.5.3 The %RSD for each target or system monitoring compound must be less than or equal to the compound's maximum acceptable %RSD listed in Table 5.

9.3.5.4 Up to two compounds may fall outside the criteria listed in Sections 9.3.5.2 and 9.3.5.3 and still meet the minimum response factor and %RSD requirements. However, these compounds must have a minimum RRF greater than or equal to 0.010, and the %RSD must be less than or equal to 40.0 percent.

9.3.5.5 Excluding those ions in the solvent front and the combined xylenes 200 µg/L standard, no quantitation ion may saturate the detector. Follow the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.3.6 Corrective Action for Initial Calibration

9.3.6.1 If the initial calibration technical acceptance criteria are not met, inspect the entire analytical system for problems. It may be necessary to clean the ion source, change the column, service the

purge and trap device or take other corrective actions to achieve the technical acceptance criteria.

9.3.6.2 Initial calibration technical acceptance criteria **must** be met before any samples or required blanks are analyzed. Any samples, QC samples or required blanks analyzed when the initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample technical acceptance criteria.

9.3.6.3 Sample analyses reported with a non-compliant initial calibration after reanalysis shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

9.4 Initial Calibration Verification

9.4.1 Summary of Initial Calibration Verification

9.4.1.1 Prior to the analysis of samples, QC samples, required blanks and after the GC/MS instrument performance check solution criteria and initial calibration technical criteria have been met, the initial calibration must be verified with a separate source standard.

9.4.1.2 If the technical acceptance criteria for the initial calibration verification are not met, then the Contractor must stop and correct the problem before continuing the analytical sequence.

9.4.2 Frequency of Initial Calibration Verification

9.4.2.1 A second source verification of the initial calibration curve must be performed by the Contractor upon award of the contract, whenever an initial calibration is performed and whenever the Contractor takes corrective action which may change or affect the initial calibration criteria (e.g., ion source cleaning or repair, column replacement, etc.).

9.4.3 Procedure for Initial Calibration Verification

9.4.3.1 Analyze the initial calibration verification standard prepared in Section 7.2.4.6 following the sample analysis procedure in Section 9.1.4.

9.4.3.2 The initial calibration verification standard must be analyzed using the same conditions established for the initial calibration. There will be separate calibration verification data for the heated and the unheated purge analyses.

9.4.4 Calculations for Initial Calibration Verification

9.4.4.1 Calculate the relative response factor (RRF) for each volatile target and system monitoring compound using Equation 1.

9.4.4.2 Calculate the percent difference between the initial calibration verification standard relative response factor and the most recent initial calibration mean relative response factor for each purgeable target and system monitoring compound using Equation 4.

EQ. 4

$$\%Difference = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

Where,

RRF_c = Relative response factor from initial calibration verification standard.

$\overline{RRF}_i$ = Mean relative response factor from the most recent initial calibration meeting technical acceptance criteria.

Note: The initial calibration verification results must be reported on an appropriate form and must be included in the data package with the associated initial calibration data.

9.4.5 Technical Acceptance Criteria for the Initial Calibration Verification

9.4.5.1 The initial calibration verification standard must be analyzed at the concentration level described in Section 7.2.4.7.2, and at the frequency described in Section 9.4.2 on a GC/MS system meeting the GC/MS Instrument Performance check and initial calibration technical acceptance criteria.

9.4.5.2 The relative response factor (RRF) for each purgeable target and system monitoring compound must be greater than or equal to the compounds's minimum acceptable response factor listed in Table 5.

9.4.5.3 The relative response factor percent difference (%D) for each purgeable target and system monitoring compound must be less than or equal to $\pm$ 30.0 percent.

9.4.5.4 Up to two compounds may fail the requirements listed in Sections 9.4.5.2 and 9.4.5.3 and still meet the minimum relative response factor criteria and percent difference criteria. However, these compounds must have a minimum relative response factor greater than or equal to 0.010 and the percent difference must be within the inclusive range of $\pm$ 40.0 percent.

9.4.5.5 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.4.6 Corrective Action for Initial Calibration Verification

9.4.6.1 If the initial calibration verification technical acceptance criteria are not met, reanalyze and check the initial calibration verification standard following Sections 9.4.3 and 9.4.4. If the reanalysis meets the technical acceptance criteria established in Section 9.4.5, then proceed with sample analysis.

9.4.6.2 If the reanalysis still does not meet the technical acceptance criteria, examine the preparation procedures and calculations which were used to make the initial calibration and initial calibration verification solutions. If the procedures or calculations were incorrect, correct the calculations and verify the technical acceptance criteria. It may be necessary to take other corrective actions to achieve the initial calibration technical acceptance criteria.

9.4.6.3 Initial calibration verification technical acceptance criteria **must** be met before any samples, QC samples, or required blanks are analyzed. Any continuing calibrations, samples, QC sample or required blanks analyzed when the initial calibration verification technical acceptance criteria have not been met must be reanalyzed at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample technical acceptance criteria.

9.4.6.4 Sample results reported with a non-compliant initial calibration verification standard after reanalysis shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

9.5 Continuing Calibration

9.5.1 Summary of Continuing Calibration

9.5.1.1 Prior to the analysis of samples and required blanks and after GC/MS Instrument Performance check, initial calibration and initial calibration verification technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing a continuing calibration standard containing all the purgeable target and system monitoring compounds to ensure that the instrument continues to meet the instrument sensitivity and the stability of the mid point response requirements of the SOW.

9.5.1.2 If the technical acceptance criteria for continuing calibrations are not met, then the contractor must stop and correct the problem before continuing the analytical sequence.

9.5.2 Frequency of Continuing Calibration

9.5.2.1 A check of the calibration curve must be performed once every 12 hours (see Section 9.2.2 for the definition of the 12-hour time period). If time remains in the 12-hour time period after meeting the initial calibration technical acceptance criteria, samples may be analyzed. It is not necessary to analyze a continuing calibration standard if the initial calibration standard that is the same concentration as the continuing calibration standard meets the continuing calibration technical acceptance criteria. A method blank is required. Quantify all sample results against the initial calibration standard that is the same concentration as the continuing calibration standard (50 µg/L for all the TCL and SMCs except 100 µg/L for tetrahydrofuran and 250 µg/L for 1,4-dioxane).

9.5.2.2 If time does **not** remain in the 12-hour period beginning with the analysis of the GC/MS instrument performance check solution, a new analysis of the GC/MS instrument performance check solution must be made. If the reanalysis meets the ion abundance criteria for BFB, then a continuing calibration standard may be analyzed.

9.5.3 Procedure for Continuing Calibration

9.5.3.1 Analyze the continuing calibration standard prepared in Section 7.2.4.7.3 according to Section 9.1.4.

9.5.3.2 NOTE: Separate initial and continuing calibrations must be performed for water samples and low level soil/sediment samples (unheated purge vs. heated purge). Extracts of medium level soil/sediment or waste samples may be analyzed using the calibrations for water samples.

9.5.4 Calculations for Continuing Calibration

9.5.4.1 Calculate the relative response factor (RRF) for each target and system monitoring compound using Equation 1.

9.5.4.2 Calculate the percent difference between the continuing calibration relative response factor and the most recent initial calibration mean relative response factor for each purgeable target and system monitoring compound using Equation 4. Note: If the midpoint standard of the initial calibration is used as the daily standard then these continuing calibration calculations must be performed and reported on a Form VIII/VOA.

9.5.5 Technical Acceptance Criteria for Continuing Calibration

9.5.5.1 The continuing calibration standard must be analyzed at the frequency described in Section 9.4.2 on a GC/MS system meeting the GC/MS Instrument Performance Check, initial calibration and initial calibration verification technical acceptance criteria.

9.5.5.2 The relative response factor (RRF) for each purgeable target and system monitoring compound must be greater than or equal to the compound's minimum acceptable response factor listed in Table 5.

9.5.5.3 The relative response factor percent difference (%D) for each purgeable target and system monitoring compound must be less than or equal to the compounds maximum acceptable %D listed in Table 5.

9.5.5.4 Up to two compounds may fail the requirements listed in Sections 9.4.5.2 and 9.4.5.3 and still meet the minimum relative response factor criteria and percent difference criteria. However, these compounds must have a minimum relative response factor greater than or equal to 0.010 and the percent difference must be within the inclusive range of ±40.0 percent.

9.5.5.5 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.5.6 Corrective Action for Continuing Calibration

9.5.6.1 If the continuing calibration technical acceptance criteria are not met, recalibrate the GC/MS instrument according to Section 9.3.3. It may be necessary to clean the ion source, change the column or take other corrective actions to achieve the continuing calibration technical acceptance criteria.

9.5.6.2 Continuing calibration technical acceptance criteria **must** be met before any samples, QC samples, or required blanks are analyzed. Any samples, QC samples or required blanks analyzed when continuing calibration technical acceptance criteria have not been met must be reanalyzed no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample technical acceptance criteria.

9.5.6.3 Sample analyses reported with a non-compliant continuing calibration after reanalysis shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample weight/volume (less than 90% of the required weight/volume) is received to perform the analyses, the Contractor shall contact the RSCC for instructions. The Region will either require that sample analyses not be performed or will require that a reduced volume be used for the sample analysis. Changes in the sample analysis must be preapproved by the Region. The Contractor shall document the problem, EPA sample numbers for the affected samples, and the Regional instructions (including sample weight/volume prepared and analyzed) in the SDG Narrative.

10.1.2 If multiphase samples (e.g., two-phase liquid sample, oily sludge/sandy soil sample) are received by the Contractor, then the Contractor shall notify the RSCC that a multiphase sample has been received. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do one of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample and analyze each phase separately. RSCC will provide EPA sample numbers for the additional phases, if required.
- Separate the phases of the sample and analyze one or more of the phases, but not all of the phases. RSCC will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope of the method), then the Region may require the Contractor to do one of the following:

- Separate the phases and analyze the phase(s) that are amenable to analysis. RSCC will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the problem, the EPA sample numbers for the affected samples, and the Regional instructions in the SDG Narrative.

10.1.3 Aqueous Samples

10.1.3.1 pH Determination (Aqueous Samples)

Once the sample aliquots have been taken from the VOA vial, the pH of the aqueous sample must be determined. The purpose of the pH determination is to ensure that all VOA samples were acidified in the field. Test the pH by placing one or two drops of sample on the pH paper (do **not** add pH paper to the vial). Record the pH of each sample and report on the Form I/VOA.

10.1.3.2 All water samples must be allowed to warm to ambient temperature before analysis.

10.1.3.3 Prior to the analysis of samples, establish the appropriate purge and trap GC/MS operating conditions, as outlined in Section 9.1, analyze the GC/MS instrument performance check solution (9.2), and calibrate the GC/MS system according to Sections 9.3 through 9.5. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and sample.

10.1.3.4 If time remains in the 12-hour period (as described in Section 9.3.2), samples may be analyzed without analysis of a continuing calibration standard.

10.1.3.5 If time does **not** remain in the 12-hour period since the injection of the GC/MS instrument performance check solution, both the GC/MS instrument performance check solution(section 9.2) and the continuing calibration standard (section 9.5) must be reanalyzed and must meet technical acceptance criteria before sample analysis may begin.

10.1.3.6 Prior to sample analysis and after initial and/or continuing calibration technical acceptance criteria have been met, the GC/MS system must be demonstrated to be free of contamination by the analysis of instrument and method blanks as specified in Sections 12.1.2 and 12.1.3. All technical acceptance criteria for blank analyses defined in Section 12.1.4 must be met before proceeding with sample analyses.

10.1.3.7 Analyze a 5 ml aliquot of the aqueous sample according to Section 9.1.4.

10.1.3.7.1 If foaming is noted at the onset of purging, then the Contractor shall stop the sample analysis and contact the RSCC to obtain instructions. The Region may instruct the contractor to do one of the following:

- Add an antifoaming agent to the sample and analyze a method blank that has been spiked with the same amount of antifoaming agent that was added to the sample.
- Do not analyze the sample.
- Analyze the sample at a specified dilution.

10.1.3.7.2 No other changes in the analyses will be permitted. The Contractor shall document the problem, the EPA sample numbers for the affected samples and the Regional instructions in the SDG Narrative.

10.1.3.8 Proceed with Data Analysis and Calculations as described in Section 11.0. All sample technical acceptance criteria (Section 11.4) must be met before sample results are reported.

10.1.4 Percent Moisture Determination

Prior to initiating sample analysis, determine the sample's percent moisture. Weigh 5 - 10 g of the soil/sediment/solid into a tared crucible and dry overnight or for at least 12 hours in an oven at 105 °C. Allow the sample to cool in a desiccator before reweighing. Calculate the percent moisture using the equation below. Concentrations of individual compounds will be reported relative to the dry weight of soil/sediment/solid.

EQ. 5

$$\%moisture = \frac{g\ of\ wet\ sample - g\ of\ dry\ sample}{g\ of\ wet\ sample} \times 100$$

10.1.4.2 If solid matrix samples contain percent moisture greater than or equal to 70 percent ($\geq$ 70 %), a larger volume of sample must be analyzed to achieve the dry weight CRQLs listed in Exhibit C. The equation for calculating the increased sample weight when percent moisture is equal to or greater than 70 percent is given below:

EQ. 6

$$Sample\ Weight = 5.0\ g \times \frac{\%moisture}{100} + 5\ g$$

10.1.4.3 If a sufficient sample weight/volume has not been provided by the sampler to analyze an increased portion of sample, then the Contractor shall contact the RSCC to ascertain whether the or not the sample should be analyzed. For all samples that do not meet the percent moisture requirement, the Contractor shall note the problem, the EPA sample numbers for the affected samples, the % moisture and sample weight prepared and analyzed in the SDG Narrative.

10.1.4.4 If it is not possible to increase the sample size, contact the RSCC for direction. The Region may require that the sample not be analyzed or another method of analysis may be required.

10.1.4.5 If percent moisture is determined to be $\geq$ 90 percent, then the Contractor must contact the RSCC for directions. The Region may request that the samples not be analyzed or another method of analysis may be required.

10.1.4.6 The Contractor must determine whether a soil/sediment/solid sample should be analyzed by the low or medium method. It is the responsibility of the Contractor to analyze the sample at the correct level.

10.1.4.7 Four approaches may be taken to determine whether the low level or medium level method must be followed.

- Assume the sample is low level and analyze a 5 g sample or adjusted sample weight determined above.
- Use an in-house laboratory screening procedure. This procedure must be documented and available for review during on-site laboratory evaluation or when requested by the Region.
- Use the X factor calculated from the hexadecane screen (Appendix A) to determine the appropriate method for analysis.
- The field sampler may indicate the level on the chain-of-custody submitted with the samples.

Note: The screening data must be provided in the sample data package. The data must be clearly labeled with the EPA sample number, reference standard concentration and amount injected to justify the level of analysis performed.

10.1.4.8 If the on column concentration of any TCL compound exceeds the initial calibration range from the analysis of a low level sample (5 g) the medium level method must be used.

10.1.5 Low Level Soil/Sediment/Solid Samples

The low level soil/sediment/solid method is based on a heated purge of a soil/sediment/solid sample mixed with reagent water containing the system monitoring compounds and the internal standards. Analyze all QC samples, blanks and standards under the same conditions as the samples.

10.1.5.1 Use 5 grams or 5 g dry weight equivalent of sample, or your in-house screening procedure or use the X Factor (Appendix A) to determine the level for sample analysis.

Note: The sample weight can be a fixed weight which cannot be altered. The soil samples may be submitted in glass vials with preservative or in Encore™ samplers or equivalent.

10.1.5.2 Prior to the analysis of samples, establish the appropriate purge and trap GC/MS operating conditions, as outlined in Section 9.1, analyze the GC/MS instrument performance check solution (9.2), and calibrate the GC/MS system according to Sections 9.3 through 9.5. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and sample. The low level

soil instrumentation and procedures must be used for calibration and quantitation of the low level soil samples.

10.1.5.3 Prior to sample analysis and after calibration technical acceptance criteria have been met, the GC/MS system must be demonstrated to be free of contamination by the analysis of instrument and method blanks as specified in Section 12.1.2 and 12.1.3. All technical acceptance criteria for blank analyses defined in Section 12.1.4 must be met before proceeding with sample analyses.

10.1.5.4 Refer to Appendix B, Section 9.0 for the low soil sample procedure.

10.1.5.5 The sample (for volatile organics) is defined as the entire contents of the sample container. Use a calibrated top loading balance. Note and record the actual weight to the nearest 0.1 g in the sample preparation log sheet and on the Form I-VOA.

10.1.5.6 Add the spiked reagent water (Section 10.1.4.13) to the purge device and analyze the sample on the purge and trap system.

10.1.5.7 NOTE: The steps in Sections 10.1.4.13 and 10.1.4.14 above must be performed rapidly to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

10.1.5.8 Heat the sample to 40 °C (± 1 °C) for 1.5 minutes and purge the sample for 11.0 ± 0.1 minutes.

10.1.5.9 Proceed with sample analysis as outlined in Section 9.1.4.3 and 9.1.4.4

10.1.6 Medium Level Soil/Sediment/Solid Samples

10.1.6.1 The medium level soil/sediment/solid method is based on extracting the soil/sediment/solid sample with methanol. An aliquot of the methanol extract is added to reagent water containing the system monitoring compounds and the internal standards. The reagent water containing the methanol extract is purged at ambient temperature. When using the screening method in Appendix A, all samples with an X Factor > 1.0 should be analyzed by the medium level method.

10.1.6.2 Prior to the analysis of samples, establish the appropriate purge and trap GC/MS operating conditions, as outlined in Section 9.1, analyze the GC/MS instrument performance check solution (9.2), and calibrate the GC/MS system according to Sections 9.3 through 9.5. This should be done prior to the addition of the methanol extract to reagent water. Because the methanol extract and reagent water mixture is purged at ambient temperature, the GC/MS instrument performance check, initial calibration, and continuing calibration for water samples may be used for analyses of medium level soil/sediment/solid sample extracts.

10.1.6.3 The sample is defined as the entire contents of the sample container. Do not discard any supernatant liquids. The vial may be prepared in the field but laboratory preparation may be required if Encore™ samplers or equivalent are used for sampling. Approximately 5.0 g of sample is added to a tared 15 mL vial. Use a top loading balance. Note and record the actual weight to the nearest 0.1 g. The sample weight will be provided on the vial if the field sampler has prepared the samples in the field. But the laboratory must also weigh the sample vials and immediately report all discrepacies to the Regional Sample Control Coordinator.

10.1.6.4 Quickly add 10 mL of methanol to the vial. Cap and shake gently by hand for 2 minutes.

10.1.6.5 NOTE: The steps in Sections 10.1.5.3 and 10.1.5.4 must be performed rapidly to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

10.1.6.6 Let the solution settle. Then, using a disposable pipette, transfer approximately 1 mL of extract into a GC vial for storage. The remainder may be discarded. The 1 mL extract may be stored in the dark at 4 °C (± 2 °C) prior to the analysis.

If the samples are prepared in the field than the laboratory must shake the vial gently for 2 minutes and transfer a 1 mL aliquot into a GC vial for storage within 24 hrs. of sample receipt.

10.1.6.7 Table 6 can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. If the hexadecane screen procedure (Appendix A) was followed, use the estimated concentration (Option A) or the X Factor (Option B) to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low level analysis or from the in-house screening procedure to determine the appropriate volume.

10.1.6.8 To prepare the spiked reagent water for soil/sediment samples, remove the plunger from a 5 mL "Luerlok" type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water. Vent trapped air through the syringe valve and adjust the volume to 4.9 mL. Pull the plunger back to 5 mL to allow volume for the addition of sample extract and standards. Add 10 μL of system monitoring compound spiking solution (Section 7.2.4.1) and 10 µL of the internal standard solution (Section 7.2.4.3). Also add the volume of methanol extract determined in Section 10.1.5.7 and a volume of clean methanol to total 100 µL (excluding methanol in system monitoring/internal standard solutions).

10.1.6.9 Attach the syringe-syringe valve assembly to the syringe valve on the purge device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

10.1.6.10 Proceed with the GC/MS analysis as outlined in Section 9.1.

10.1.7 Oily Sludge Samples

10.1.7.1 Oily sludge samples are reported on a wet weight (as is) basis.

10.1.7.2 The oily sludge method is based on extracting the sludge with methanol or, if the sludge sample is soluble in methanol, diluting the sludge in methanol. An aliquot of the methanol extract or diluent is then added to 5 mL reagent water containing the system monitoring compounds and the internal standards. The reagent water containing the methanol extract or diluent is purged at ambient temperature.

10.1.7.3 Prior to the analysis of samples, establish the appropriate purge and trap GC/MS operating conditions, as outlined in Section 9.1, analyze the GC/MS instrument performance check solution (9.2), and calibrate the GC/MS system according to Sections 9.3 through 9.5. This should be done prior to the addition of the methanol extract (diluent) to reagent water. Because the methanol extract (diluent) and reagent water mixture is purged at ambient temperature, the instrument performance check, initial calibration and continuing calibration for water samples may be used for analyses of oily sludge extracts and diluents.

10.1.7.4 Oily Sludge Sample Size

10.1.7.4.1 Non-soluble Oily Sludge

The sample (for volatile organics) is defined as the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh 5 g (wet weight) of oily waste that is not soluble in methanol into a tared 15 mL vial. Use a calibrated top loading balance. Note and record the actual weight to the nearest 0.1 g.

10.1.7.4.2 Soluble Oily Sludge

The sample (for volatile organics) is defined as the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh 1 g (wet weight) of oily waste that is soluble in methanol into a tared 15 mL vial. Use a calibrated top loading balance. Note and record the actual weight to the nearest 0.1 g.

10.1.7.5 Quickly add 10 mL of methanol to the vial. Cap and shake gently by hand for 2 minutes.

10.1.7.6 NOTE: The steps in Sections 10.1.6.3 and 10.1.6.4 must be performed rapidly to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

10.1.7.7 Let the solution settle. Then, using a disposable pipette, transfer approximately 1 mL of extract/diluent into a GC vial for storage. The remainder may be discarded. The 1 mL extract/diluent must be stored in the dark at 4 °C (± 2 °C) prior to analysis.

10.1.7.8 Remove the plunger from a 5 mL "Luerlok" type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water. Vent trapped air through the syringe valve and adjust the volume to 4.9 mL. Pull the plunger back to 5 mL to allow volume for the addition of sample and standards. Add 10 μL of system monitoring compound spiking solution (Section 7.2.4.1) and 10 µL of the internal standard solution (Section 7.2.4.3). Add 100 µl of the methanol extract/diluent (Section 10.1.6.7).

Note: For highly contaminated samples, secondary dilutions may be necessary. For each analysis, the sample volume plus clean methanol added to 5 ml of reagent water must total 100 µL.

10.1.7.9 Attach the syringe-syringe valve assembly to the syringe valve on the purge device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

10.1.7.10 Proceed with the GC/MS analysis as outlined in Section 9.1.4.3 and 9.1.4.4

10.1.8 Sample Dilutions

10.1.8.1 For medium level soil/sediment/solid analyses and oily sludge analyses, the purgeable organics screening procedure (Appendix A), if used, will show the approximate concentrations of major sample components. If a dilution of the sample was indicated, this dilution shall be made just prior to GC/MS analysis of the sample. All steps in the dilution procedure must be performed without delays until the point at which the diluted sample is in a gas tight syringe.

10.1.8.2 If the on-column concentration of any target compound in any sample saturates the detector, a new aliquot of that sample must be diluted and purged. Guidance in performing dilutions and exceptions to this requirement are given in Sections 10.1.7.3 through 10.1.7.9.

10.1.8.3 Use the results of the original analysis to determine an approximate dilution factor required to get the largest target compound peak within the initial calibration range.

10.1.8.4 The dilution factor chosen should keep the response of the largest peak for a target compound in the upper half of the initial calibration range of the instrument.

10.1.8.5 Dilutions for water samples are performed in volumetric flasks (10 mL to 100 mL).

Note: Dilutions cannot be made to Low Soil samples.

10.1.8.6 Volumetric Dilution

10.1.8.6.1 Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions. However, the Contractor must make every effort to minimize the number of dilutions in order to minimize potential dilution errors.

10.1.8.6.2 Calculate the approximate volume of reagent water which will be added to the volumetric flask selected and add slightly less than this quantity of reagent water to the flask.

10.1.8.6.3 For water samples, inject the proper aliquot from the syringe prepared in Section 9.1.4.2.1 into the volumetric flask. Aliquots of less than 1 mL increments are prohibited. Dilute the flask to the mark with reagent water. Cap the flask, invert, and shake three times.

10.1.8.6.4 Fill a 5 mL syringe with the diluted sample as in Section 9.1.4.2.1.

10.1.8.6.5 If this is an intermediate dilution, use it and repeat the above procedure to achieve larger dilutions.

10.1.8.7 Do **not** submit data for more than two analyses, i.e., the original sample and **one** dilution, or the most concentrated dilution analyzed and one further dilution.

10.1.8.8 For total xylenes, where three isomers are quantified as two peaks, the calibration of each peak should be considered separately, i.e., a diluted analysis is **not** required for total xylenes unless the concentration of the peak representing the single isomer exceeds 200 µg/L (µg/kg for solid matrices) or the peak representing the two co-eluting isomers on the GC column exceeds 400 µg/L (µg/kg for solid matrices). All other isomers must be chromatographically separated. Therefore, each isomeric peak must not exceed the upper limit of the initial calibration range.

10.1.8.9 The Contractor may receive instructions with the sampling paperwork which prohibits sample dilutions under any circumstances. This may be required in instances where the CRQLs for most target compounds must be achieved even though one or more target compounds exceed the calibration range and/or high concentrations of non-target compounds are present. In these cases, if screening results indicate that sample dilution is required to avoid detector saturation due to target and/or non-target compound ions, then the contractor shall contact the RSCC to ascertain whether or not that sample should be analyzed at a dilution. For all samples affected by this situation, the Contractor shall note the problem, the EPA sample numbers affected by this situation, and the Regional instructions in the SDG Narrative.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Compounds

11.1.1.1 The compounds listed in the Target Compound List (TCL) in Exhibit C (Volatiles) shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected target compound. Two criteria must be satisfied to verify target compound identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

11.1.1.2 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For reference, the standard must be run in the same 12-hour time period as the sample. If samples are analyzed during the same 12-hour time period as the initial calibration standards, use the RRT values from the 50 µg/L standard. If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

11.1.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, **only** if the Contractor's GC/MS meets the daily GC/MS instrument performance check technical acceptance criteria. These standard spectra must be obtained from the run used to obtain reference RRTs.

11.1.1.4 The requirements for qualitative verification by comparison of mass spectra are as follows:

- All ions present in the standard mass spectrum at a relative intensity greater than 10.0 percent (most abundant ion in the spectrum equals 100.0 percent) **must** be present in the sample spectrum.
- The relative intensities of ions specified above must agree within ± 20.0 percent between the standard and sample spectra. (Example: For an ion with an abundance of 50.0 percent in the standard spectrum, the corresponding sample abundance for that ion must be between 30.0 and 70.0 percent).
- Ions greater than 10.0 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. All compounds meeting the identification criteria must be reported with their spectra. For all compounds with positive matches that are detected below the CRQL, report the actual value followed by a "J", e.g., "3J".

11.1.1.5 If a compound cannot be verified by all of the criteria in 11.1.1.4 but, in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then the Contractor shall report that identification on the Form I qualified with an "X". The Contractor must note this decision in the SDG Narrative and proceed with quantitation as described in Section 11.2.

11.1.2 Identification of Non-Target Compounds

11.1.2.1 A library search shall be executed for non-target sample components for the purpose of tentative identification. The NIST/EPA/NIH (May 1992 release or most recent release) and/or

Wiley (1991 release or most recent release), or equivalent mass spectral library, shall be used.

11.1.2.2 Up to 10 organic compounds of greatest apparent concentration not listed in Exhibit C for the volatile and semivolatile fraction, excluding the system monitoring compounds and internal standard compounds, shall be identified tentatively via a forward search of the NIST/EPA/NIH (May 1992 release or most recent release) and/or Wiley (1991 release or most recent release), or equivalent mass spectral library. The following are not to be reported: 1) Substances with responses less than 10 percent of the nearest internal standard free of interferences (as determined by inspection of the peak areas or height), 2) Substances, which elute earlier than 30 seconds before the first purgeable compound listed in Exhibit C (Volatiles) or three minutes after elution of the last purgeable compound listed in Exhibit C (Volatiles), are not required to be searched in this fashion, 3) Carbon dioxide, and 4) Semivolatile TCL compounds listed in Exhibit C). The mass spectral interpretation specialist will assign a tentative identification only after visual comparison of the sample spectrum with all the library search spectra.

11.1.2.3 NOTE: Computer generated library search routines must not use normalizations which would misrepresent the library or unknown spectra when compared to each other.

11.1.2.4 Guidelines for making tentative identification:

11.1.2.4.1 Relative intensities of major ions in the reference spectrum (ions greater than 10.0 percent of the most abundant ion) should be present in the sample spectrum.

11.1.2.4.2 The relative intensities of the major ions should agree within ± 20.0 percent of the reference and sample spectra. (Example: For an ion with an abundance of 50.0 percent of the reference spectrum, the corresponding sample ion abundance must be between 30.0 and 70.0 percent.)

11.1.2.4.3 Molecular ions present in reference spectrum should be present in sample spectrum.

11.1.2.4.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

11.1.2.4.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

11.1.2.5 If, in the technical judgment of the mass spectral interpretation specialist, no valid tentative identification can be made, then the compound should be reported as **unknown**. The mass spectral interpretation specialist should give additional classification of the unknown compound, if possible (i.e., unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, then the mass spectral interpretation specialist should include them on the Form I VOA-TIC and provide discussion in the SDG Narrative.

11.2 Calculations

11.2.1 Target Compounds

11.2.1.1 Target compounds which meet the identification criteria in Section 11.1, shall be quantified by the internal standard method using the equations below. The internal standard used shall be that which is assigned in Table 3. The relative response factor (RRF) from the continuing calibration standard shall be used to calculate the concentration of that target compound in the sample.

11.2.1.2 Water

EQ. 7

$$Concentration\ \mu g/L = \frac{(A_x)(I_s)(Df)}{(A_{is})(RRF)(V_o)}$$

Where,

A_x = Area of the characteristic ion (EICP) for the compound to be measured (see Table 2),
A_{is} = Area of the characteristic ion (EICP) for the specific internal standard (see Tables 3 and 4),
I_s = Amount of internal standard added in nanograms (ng),
RRF = Relative response factor from the ambient temperature purge of the calibration standard,
V_o = Volume of water purged in milliliters (mL),
Df = Dilution factor. The dilution factor for analysis of water samples for volatiles by this method is defined as the ratio of the number of milliliters (mL) of water purged (i.e., V_o above) to the number of mL of the original water sample used for purging. For example, if 2.0 mL of sample is diluted to 5 mL with reagent water and purged, Df = 5 mL/2.0 mL = 2.5 If no dilution is performed, Df = 1.

11.2.1.3 Low Soil/Sediment/Solid

EQ. 8

$$Concentration\ \mu g/Kg\ (dry\ weight\ basis) = \frac{(A_x)(I_s)}{(A_{is})(RRF)(W_s)(D)}$$

Where,

A_x, I_s, A_{is} are as given for water.
RRF = Relative response factor from the heated purge of the calibration standard,
$D = \frac{100 - \%\ moisture}{100}$
W_s = Weight of sample added to the purge tube, in grams (g),

11.2.1.4 Medium Soil/Sediment/Solid or Oily Sludge

EQ. 9

$$Concentration\ \mu g/Kg\ (Dry\ weight\ basis) = \frac{(A_x)(I_s)(V_t)(1000)(Df)}{(A_{is})(RRF)(V_a)(W_s)(D)}$$

Where,

A_x, I_s, A_{is} are as given for water.
RRF = Relative response factor from the ambient temperature purge of the calibration standard,
V_t = Total volume of the methanol extract in milliliters (mL), NOTE: This volume is typically 10 mL, even

though only 1 mL is transferred to the vial in Section 10.1.5.6,

V_a = Volume of the aliquot of the sample methanol extract (i.e., sample extract not including the methanol added to equal 100 µL) in microliters (µL) added to reagent water for purging,

W_s = Weight of soil/sediment/solid or oily sludge extracted, in grams (g),

$$D = \frac{100 - \%\ \text{moisture}}{100}$$

Df = Dilution factor. The dilution factor for analysis of soil/sediment/solid and oily sludge samples for volatiles by the medium level method is defined as:

$$\frac{\mu L\ \text{concentrated extract} + \mu L\ \text{clean solvent}}{\mu L\ \text{concentrated extract used to make dilution}}$$

The dilution factor is equal to 1.0 in all cases other than those requiring dilution of the sample methanol extract (V_t). Dilution of the extract is required when the X factor (Section 10.1.5.7) is $\geq$ 12.5. The factor of 1,000 in the numerator converts the value of V_t from mL to µL.

11.2.1.5 For water, low level and medium level soil/sediment/solid, and oily sludge samples, xylenes (o-,m- and p-isomers) are to be reported as xylenes (total). Because the m- and p-xylene isomers co-elute on capillary columns, special attention must be given to the quantitation of the xylenes. The relative response factor (RRF) determined in Section 9.4.4 is based on the peak that represents the single isomer on the GC column used, O-xylene on capillary columns. In quantitating sample concentrations, use the areas on both peaks and the RRF from Section 9.4.4. The areas of the two peaks may be summed, and the concentration determined, or the concentration represented by each of the two peaks may be determined separately, and then summed. It is required that all three xylene isomers be present in the initial and continuing calibration standards.

11.2.1.6 All other isomers must be chromatographically separated. Relative response factors must be determined for each isomer.

11.2.1.7 Secondary ion quantitation is allowed **only** when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons and the EPA sample numbers in the SDG Narrative. A secondary ion cannot be used unless a relative response factor is calculated using that secondary ion.

11.2.1.8 The requirements listed in 11.2.1.9 and 11.2.1.10 apply to all standards, samples, QC samples, and blanks.

11.2.1.9 It is expected that situations will arise where the automated quantitation procedures in the GC/MS software provide inappropriate quantitations. This normally occurs when there is compound co-elution, baseline noise, or matrix interferences. In these circumstances the Contractor must perform a manual quantitation. Manual quantitations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific TCL compound. The area integrated shall not include baseline background noise. The area integrated shall not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Any instances of manual integration and the EPA sample numbers must be documented in the SDG Narrative.

11.2.1.10 In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initialing and dating the changes made to the report, and the GC/MS operator must include the integration scan range on the report. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all compounds listed in Exhibit C (Volatiles), internal standards and system monitoring compounds.

11.2.2 Non-Target Compounds

11.2.2.1 An estimated concentration for non-target compounds tentatively identified shall be determined by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

11.2.2.2 The formulas for calculating concentrations are the same as in Sections 11.2.1.2, 11.2.1.3, and 11.2.1.4. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A relative response factor (RRF) of one (1) is to be assumed. The resulting concentration shall be qualified as "J" (estimated, due to lack of a compound-specific response factor), and "N" (presumptive evidence of presence), indicating the quantitative and qualitative uncertainties associated with this non-target component. An estimated concentration must be calculated for all tentatively identified compounds as well as those identified as unknowns.

11.2.3 CRQL Calculations

Sample specific CRQLs must be calculated and reported on VOA Form Is. If the adjusted CRQL is less than the CRQL listed in Exhibit C (Volatiles), report the CRQL listed in Exhibit C (Volatiles).

11.2.3.1 Water

EQ. 10

$$\underset{CRQL}{Adjusted} = \underset{CRQL}{Contract} \times \frac{V_x}{V_o} \times Df$$

Where,

V_o and Df are as given in Equation 7
V_x = Contract Sample Volume (5 ml)

11.2.3.2 Low Level Soil/Sediment/Solid

EQ. 11

$$\underset{CRQL}{Adjusted} = \underset{CRQL}{Contract} \times \frac{(W_x)}{(W_s)(D)}$$

Where,

W_s and D are as given in Equation 8
W_x = Contract Sample Weight (5 g)

11.2.3.3 Medium Level Soil/Sediment/Solid or oily sludge

EQ. 12

$$\underset{CRQL}{Adjusted} = \underset{CRQL}{Contract} \times \frac{(W_x)(V_t)(V_y)(Df)}{(W_s)(V_c)(V_a)(D)}$$

Where,

V_t, Df, W_s, V_a and D are as given in Equation 9
W_x = Contract Sample Weight (4 g, or 1 g for soluble oily sludge)
V_y = Contract Soil Aliquot Volume from soil methanol extract (100 µl)
V_c = Contract Soil Methanol Extract Volume (10,000 µl)

11.2.4 System Monitoring Compound Recoveries

11.2.4.1 Calculate the concentrations of the system monitoring compounds in all samples, blanks, and QC samples using the same equations that are used for calculating target compound concentrations (Section 11.2.1).

11.2.4.2 Calculate the recovery of each system monitoring compound in all samples, blanks and QC samples using Equation 13, below. Determine if the recoveries are within the technical acceptance criteria listed in Table 7, and report on Form II as specified in Exhibit B.

EQ. 13

$$\%Recovery = \frac{Concentration\ (amount)\ found}{Concentration\ (amount)\ spiked} \times 100$$

11.2.5 Internal Standard Responses and Retention Times

Internal standard responses and retention times in all samples, blanks and QC samples must be evaluated during or immediately after data acquisition. Compare sample internal standard responses and retention times to the continuing calibration internal standard responses and retention times. For samples analyzed during the same 12-hour time period as the initial calibration standards, compare the internal standard responses and retention times against the 50 µg/L calibration standard. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, and QC sample.

11.3 Technical Acceptance Criteria for Sample Analysis

Target and non target compounds in samples are identified and reported following procedures defined in Sections 11.1 and 11.2. Sample technical acceptance criteria must be met before any sample data can be reported.

11.3.1 The samples must be analyzed on a GC/MS system meeting the GC/MS instrument performance check, initial calibration, initial calibration verification and/or continuing calibration technical acceptance criteria defined in Sections 9.3.5, 9.4.5 and/or 9.5.5, respectively.

11.3.2 The samples must be analyzed or reanalyzed within the contract required holding times defined in Section 8.3.

11.3.3 The samples must have associated method blanks, storage blanks and instrument blanks meeting the blank technical acceptance criteria defined in section 12.1.4.

11.3.4 The percent recovery of each of the system monitoring compounds in the sample must be within the technical acceptance windows listed in Table 7.

11.3.5 The response for each of the internal standards must be within the inclusive range of -50.0 percent and +100.0 percent of the EICP area of the internal standards in the most recent continuing calibration analysis or 50 µg/L initial calibration standard, if appropriate.

11.3.6 The retention time shift for each of the internal standards must be within ± 0.50 minutes (30 seconds) between the sample internal standard retention times and the most recent continuing calibration standard (or 50 µg/L initial calibration standard) internal standard retention times.

11.3.7 The relative retention time (RRT) of the target compounds and system monitoring compounds in a sample must be within ±0.06 (RRT) units of its relative retention time in the continuing calibration standard or 50 µg/L initial calibration standard, if appropriate.

11.3.8 Excluding those ions in the solvent front, no ion from a target or non-target compound may saturate the detector. No target compound concentration may exceed the upper limit of the initial calibration range unless a diluted aliquot of the sample is also analyzed according to the procedures in Section 10.1.7.

11.3.9 The Contractor must demonstrate that there is no carryover from a contaminated sample before data from subsequent analyses may be submitted. After a sample that contains a target compound at a level exceeding the initial calibration range, the Contractor must either:

- Analyze an instrument blank immediately after the contaminated sample. If an autosampler is used, an instrument blank must also be analyzed using the same purge inlet that was used for the contaminated sample. The instrument blanks must meet the technical acceptance criteria for blank analysis (see Section 12.1.4), or

- Monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample and that exceeded the calibration range. The maximum contamination criteria are as follows: the sample must not contain a concentration above the CRQL for the target compounds that exceeded the limits in the contaminated sample. If an auto-sampler is used, the next sample analyzed using the same purge inlet that was used for the contaminated sample also must meet the maximum contamination criteria. If the maximum criteria were exceeded, then all samples affected by the carryover must be reanalyzed at no additional cost to the Agency.

11.4 Corrective Action for Sample Analysis

11.4.1 Sample technical acceptance criteria must be met before data are reported. Samples contaminated from laboratory sources or sample results which failed to meet the sample technical acceptance criteria must be reanalyzed at no additional cost to the Agency.

11.4.2 Corrective actions for failure to meet GC/MS instrument performance check, initial and continuing calibration and initial calibration verification must be completed before the analysis of samples.

11.4.3 Corrective actions for failure to meet blank technical acceptance criteria must be met before the analysis of any samples.

11.4.4 Corrective actions for system monitoring compound recoveries and/or internal standard compound responses that fail to meet technical acceptance criteria are defined below.

11.4.4.1 If any of the system monitoring compound recoveries and/or internal standard compounds fail to meet technical acceptance criteria:

- Check all calculations, instrument logs, the system monitoring compound and internal standard compound spiking solutions, and the instrument operation. If the calculations were incorrect, correct the calculations and verify that the system monitoring compound recoveries and internal standard compound responses meet technical acceptance criteria.

- If the instrument logs indicate that an incorrect amount of system monitoring compound or internal standard compound spiking solution was added, then reanalyze the sample after adding the correct amount of system monitoring compound and internal standard compound spiking solutions.

- If the system monitoring compound spiking solution or internal standard compound spiking solution was improperly prepared, or concentration, and/or degradation occurred, then re-prepare the solutions and reanalyze the samples.

- If the instrument malfunctioned, correct the instrument problem and reanalyze the sample. If the instrument malfunction affected the calibration, recalibrate the instrument as per Section 9.3, before reanalyzing the sample. Verify that the system monitoring compound recoveries meet acceptance criteria.

11.4.4.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was a matrix effect, take the following corrective action steps:

- Reanalyze the sample. EXCEPTION: If system monitoring compound recoveries or internal standard compound responses in

a sample used for a matrix spike or matrix spike duplicate were outside the technical acceptance criteria, then it should be reanalyzed only if system monitoring compound recoveries and internal standard compound responses met acceptance criteria in both the matrix spike and matrix spike duplicate analyses.

- If the system monitoring compound recoveries and/or the internal standard compound responses meet the technical acceptance criteria in the reanalyzed sample, then the problem was within the Contractor's control. The contractor should make every effort to reanalyze the sample within the contract required holding times. If the reanalysis was performed within holding times, then submit data only from the reanalysis. If the reanalysis was performed outside holding times, then submit both sets of data.

- If the system monitoring compound recoveries and/or the internal standard compound responses fail to meet the acceptance windows in the reanalysis, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables using the suffixes on Exhibit B.

11.4.5 Corrective actions for system monitoring compound relative retention times and/or internal standard compound retention times outside acceptance criteria are defined below:

11.4.5.1 If any of the system monitoring compound relative retention times or internal standard compound retention times are not within their acceptance criteria defined in Sections 11.3.6 and 11.3.7, check the instrument for malfunctions. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample. If the instrument malfunction affected the calibration, recalibrate the instrument according to Section 9.3, before reanalyzing the samples.

11.4.5.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was a matrix effect, take the following corrective action steps:

- Reanalyze the sample. EXCEPTION: If the system monitoring compounds relative retention times or internal standard compounds retention times in a sample used for a matrix spike or matrix spike duplicate were outside the technical acceptance criteria, then it should be reanalyzed only if the system monitoring compounds and internal standard compounds retention times were within the acceptance criteria in both the matrix spike and matrix spike duplicate analyses.

- If the system monitoring compounds relative retention times and internal standard compounds retention times are within the acceptance criteria, then the problem was within the Contractor's control. Therefore, submit only data from the reanalysis when the system monitoring compounds relative retention times and the internal standard compounds retention times are within the acceptance limits. If the sample were reanalyzed outside the contract required holding times, then submit both sets of data.

- If the system monitoring compounds relative retention times or the internal standard compounds retention times are outside the acceptance criteria in the reanalysis, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables, using the suffixes in Exhibit B.

11.4.6 If the technical acceptance criteria for GC/MS instrument performance checks, initial and continuing calibration, initial calibration verification and method/instrument/storage blanks are not met, then the contractor must stop and correct the problem before continuing the analytical sequence. Any samples analyzed when the above

technical acceptance criteria have not been met must be reanalyzed at no additional cost to the agency. Reanalysis must be completed within the contract required holding times and must meet all technical acceptance criteria.

11.4.7 Sample analyses reported with non-compliant GC/MS instrument performance check, initial and/or continuing calibration, initial calibration verification or method/instrument/storage blanks shall be subject to a commensurate reduction in sample price or zero payment due to data rejection, depending upon the impact of the non-compliance on data usability.

12.0 QUALITY CONTROL

12.1 Blank Analyses

12.1.1 Summary -- Sample analyses must not proceed until all blank technical acceptance criteria have been met. There are three different types of blanks required by this method.

12.1.1.1 METHOD BLANK - a volume of a clean reference matrix (reagent water for water samples or a purified solid matrix for low level soil/sediment/solid samples) that is carried through the entire analytical procedure. If an anti-foaming agent is required for aqueous sample analysis, the anti-foaming agent must be added to reagent water and processed as the method blank for associated samples. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

A methanol blank is the method blank for medium level and oily sludge sample analysis. The same amount of methanol that is used in the field sample analysis is added to reagent water for analysis.

12.1.1.2 STORAGE BLANK - upon receipt of the first samples in an SDG, two 40.0 ml screw-cap volatile vials with PTFE-faced silicone septa are filled with reagent water (80 ml total). The vials are stored with the samples in the SDG under the same storage conditions. The storage blank is analyzed concurrently with the last sample in the SDG. The storage blank indicates whether contamination may have occurred during storage of samples. A storage blank must be prepared for aqueous and soil samples.

12.1.1.3 INSTRUMENT BLANK - a 5.0 ml aliquot of reagent water that is carried through the entire analytical procedure. Instrument blanks are analyzed after a sample/dilution which contains a target compound exceeding the initial calibration range or a non-target compound which either saturates the detector or produces a peak height comparable to the standard level peaks. The results from the instrument blank analysis indicate whether there is contamination from a previous sample. Instrument blanks must be analyzed to demonstrate that the purge chamber and purge and trap system are free of contamination.

12.1.2 Frequency of Blank Analyses

12.1.2.1 Method Blank - The method blank must be analyzed at least once during every 12-hour time period on each GC/MS system used for volatile analysis (see Section 9.2.2 for the definition of the 12-hour time period).

12.1.2.2 The method blank **must** be analyzed after the continuing calibration and before any samples, or QC samples are analyzed. The method blank must be analyzed after the initial calibration sequence if samples or QC samples are analyzed before the 12-hour period expires.

12.1.2.3 Storage Blank - A minimum of one storage blank must be analyzed concurrently with the last sample in the SDG.

12.1.2.4 Instrument Blank - The Contractor must demonstrate that there is no carryover from contaminated samples before data from subsequent analyses may be used. Samples/dilutions may contain target compounds at levels exceeding the initial calibration range. An instrument blank must be analyzed after the sample that exceeds the calibration range, in the same purge vessel/inlet if an autosampler is used or after a sample that meets the maximum contamination criteria noted in Section 11.3.8 must be analyzed. For these purposes, if the instrument blank meets the technical acceptance criteria for blank analyses or the sample meets the maximum contamination criteria, the system is considered to be

uncontaminated. If the instrument blank or sample does not meet the criteria (i.e., is considered to be contaminated), then the system must be decontaminated. Until an instrument blank meets the blank technical acceptance criteria or a sample meets the maximum contamination criteria described in Section 11.3.8, any samples analyzed since the original contaminated sample must be reanalyzed at no additional cost to the Agency. NOTE: Only the instrument blank which demonstrates that there was no carryover from the previous sample or the instrument blank that demonstrates that the system is clean (Section 12.1.4) needs to be reported. Instrument blanks analyzed during the instrument decontamination process which exceed the requirements listed in Section 12.1.4 do not need to be reported.

12.1.3 Procedure for Blank Analyses

12.1.3.1 For water samples, a volatile method blank consists of a 5 ml volume of reagent water (Section 7.1.1) spiked with 10 µl of the system monitoring compound spiking solution (Section 7.2.4.1) and 10 µl of the internal standard spiking solution (Section 7.2.4.3) and carried through the analytical procedure (Section 10.1.3).

12.1.3.2 For low level soil/sediment/solid samples, a volatile method blank consists of 5 g of a purified solid matrix added to 5 ml of reagent water that has been spiked with 10 µl of the system monitoring compound spiking solution (Section 7.2.4.1) and 10 µl of the internal standard spiking solution (Section 7.2.4.3). The method blank is then carried through the analytical procedure using a heated purge as described in Section 10.1.4.

12.1.3.3 For medium level soil/sediment/solid samples, a volatile method blank consists of 4 g of a purified solid matrix added to 10 ml of methanol and extracted for two minutes according to the procedure described in Section 10.1.5. A 100 μL aliquot of the methanol is added to 5 ml volume of reagent water and spiked with 10 µl of the system monitoring compound spiking solution (Section 7.2.4.1) and 10 µl of the internal standard spiking solution (Section 7.2.4.3) and taken through the analytical procedure (Section 10.1.5).

12.1.3.4 For oily sludge (waste) samples, a volatile method blank consists of a 5 ml volume of reagent water (Section 7.1.1) spiked with 10 µl of the system monitoring compound spiking solution (Section 7.2.4.1) and 10 µl of the internal standard spiking solution (Section 7.2.4.3) and 100 µl of methanol carried through the analytical procedure (Section 10.1.6).

12.1.3.5 Storage/instrument blanks consist of a 5 ml volume of reagent water, as defined in Sections 12.1.1.2 and 12.1.1.3 spiked with 10 µl of the system monitoring compound spiking solution (Section 7.2.4.1) and 10 µl of the internal standard spiking solution (Section 7.2.4.3) and carried through the analytical procedure (Section 10.1.3).

12.1.3.6 For samples requiring the addition of an anti-foaming agent (Section 10.1.3.7), a volatile anti-foaming blank consists of a 5 ml volume of reagent water (Section 7.1.1), which is spiked with 10 µl of the system monitoring compound spiking solution (Section 7.2.4.1), 10 µl of the internal standard spiking solution (Section 7.2.4.3), and an equal volume of anti-foaming agent as the field samples, and carried through the analytical procedure (Section 10.1.3).

12.1.3.7 Identify and quantitate target and non-target compounds in all blanks following the procedures outlined in Sections 11.1 and 11.2.

12.1.4 Technical Acceptance Criteria for Blank Analyses

12.1.4.1 All blanks must be analyzed on a GC/MS system meeting the GC/MS instrument performance check, initial calibration, initial calibration verification and continuing calibration technical acceptance criteria defined in Sections 9.2.4, 9.3.5, 9.4.5 and

9.5.5. All blanks must be analyzed at the frequency described in Section 12.1.2.

12.1.4.2 The percent recovery of each of the system monitoring compounds in any blank must be within the technical acceptance windows listed in Table 7.

12.1.4.3. The response for each of the internal standards in any blank must be within the inclusive range of -50.0 percent and +100.0 percent of the EICP area of the internal standards in the most recent continuing calibration analysis or 50 µg/L initial calibration standard, if appropriate.

12.1.4.4 The retention time shift for each of the internal standards must be within ± 0.50 minutes (30 seconds) between the blank internal standard retention times and the most recent continuing calibration standard (or 50 µg/L initial calibration standard) internal standard retention times.

12.1.4.5 The relative retention time (RRT) of the target compounds and system monitoring compounds in a blank must be within ±0.06 (RRT) units of its relative retention time in the continuing calibration standard or 50 µg/L initial calibration standard, if appropriate.

12.1.4.6 The concentration of each target compound found in the blank must be less than its CRQL listed in Exhibit C (Volatiles), except for methylene chloride which must be less than 2.5 times its CRQL, and acetone and 2-butanone, which must be less than 5 times the CRQL.

12.1.4.7 Non-target compounds which are found in the blanks must not interfere with target compound identification or quantitation.

12.1.5 Corrective Action for Blank Analyses

12.1.5.1 It is the Contractor's responsibility to ensure that method interferences caused by the contaminants in solvent, reagents, glassware, laboratory air and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If a Contractor's blanks exceed the technical acceptance criteria listed in Section 12.1.4.6, the Contractor must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures must be taken and documented before any further samples or QC samples are analyzed.

12.1.5.2 Any method blank or instrument blank that fails to meet the technical acceptance criteria for blank analyses must be reanalyzed at no additional cost to the Agency. Furthermore, all samples, including QC samples, processed within the 12-hour period associated with a method blank or instrument blank that does not meet the technical acceptance criteria for blanks must also be reanalyzed at no additional cost to the Agency.

12.1.5.3 If the storage blank does not meet the technical acceptance criteria for blank analyses listed in Sections 12.1.4.1 through 12.1.4.5, then correct system problems and reanalyze the storage blank. If the storage blank does not meet the technical acceptance criteria listed in Section 12.1.4.6, then reanalyze the storage blank to determine whether the contamination occurred during storage or during the analysis. If, upon reanalysis, the storage blank meets the technical acceptance criteria listed in Sections 12.1.4, then the problem occurred during the analysis and the reanalyzed storage blank results must be reported. If upon reanalysis, the storage blank did not meet the technical acceptance criteria listed in Section 12.1.4.6, then the problem occurred during storage. The laboratory manager or his/her designee must address the problem in the SDG Narrative and discuss the corrective actions implemented to prevent future occurrences. Report storage blank results on a Form I VOA, which must meet all requirements in Exhibit B and be included with the data package.

12.1.5.4 If the technical acceptance criteria for blank analyses are not met, then the contractor must stop and correct the problem before

continuing the analytical sequence. If sample analyses are reported with non-compliant blanks, then the contractor shall receive a commensurate reduction in sample price or zero payment depending upon the impact of the non-compliance on data usability.

12.2 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

12.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix and to determine the precision of the methods used for volatile analysis, the Agency has prescribed a mixture of volatile target compounds to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method.

12.2.2 Frequency of MS/MSD

12.2.2.1 A matrix spike and matrix spike duplicate must be performed for each group of samples of a similar matrix for the following, whichever is most frequent:

- Each SDG (not to exceed 20 field samples), or
- Each matrix within an SDG, or
- Each group of samples of a similar concentration level (soils only).
- EPA may require additional MS/MSD analyses, upon Regional request, for which the Contractor will be paid.

12.2.2.2 As a part of the Agency's QA/QC program, aqueous equipment and/or trip blanks (field QC) may accompany soil/sediment samples and/or water samples that are delivered to a laboratory for analysis. The Contractor shall not perform MS/MSD analysis on any of the designated field QC samples.

12.2.2.3 The Contractor shall not perform MS/MSD analysis on any designated Performance Evaluation samples.

12.2.2.4 If the EPA Region designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample volume to perform an MS/MSD, then the Contractor shall contact the RSCC to ascertain an alternate sample to be used for the MS/MSD analysis. The EPA sample numbers, Regional instructions, and date of contact must be included in the SDG Narrative.

12.2.2.5 If there is insufficient sample volume in any of the samples in an SDG to perform an MS/MSD, then the Contractor shall immediately contact the RSCC to report the problem. The Region will either approve that no MS/MSD is required, or require that a reduced sample aliquot be used for the unspiked sample and MS/MSD analysis, or that the unspiked sample is analyzed at full volume and the MS/MSD is analyzed at reduced volume. The RSCC will notify the Contractor of the resolution. The Contractor shall document the decision in the SDG Narrative.

12.2.2.6 If the Contractor has a question regarding the frequency, etc., of the MS/MSD analyses for a particular SDG, contact the RSCC for clarification.

12.2.3 Procedure for Preparing MS/MSD

12.2.3.1 Water

To prepare a matrix spike and matrix spike duplicate for water samples, add 10 µl of the matrix spiking solution (Section 7.2.4.2) to each of the two 5 ml aliquots of the sample chosen for spiking. Process samples according to Section 10.1.3. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike compound.

12.2.3.2 Low Level Soil/Sediment/Solid Matrices

To prepare a matrix spike and matrix spike duplicate for low level soil/sediment/solid samples, add 10 µl of the matrix spiking solution (Section 7.2.4.2) to the 5 ml of spiked reagent water added to each of the two aliquots of the soil/sediment/solid from the sample chosen for spiking. Process samples according to Section 10.1.4. The concentration for a 5 g sample should be equivalent to 50 µg/kg of each matrix spike compound.

Note: The percent solids content must be used to determine the appropriate spike volume.

12.2.3.3 Medium Level Soil/Sediment/Solids Matrices or Oily Sludge

12.2.3.3.1 To prepare a matrix spike and matrix spike duplicate for medium level soil/sediment/solid or oily sludge samples, add 9 ml of methanol and 1 ml of matrix spike solution to each of two aliquots of the soil/sediment/solid or oily sludge sample chosen for spiking. Prepare samples according to Section 10.1.5.1 through 10.1.5.6 for medium level soil/sediment/solid samples or Sections 10.1.6.1 through 10.1.6.7 for oily sludge samples. Add a 100 µl aliquot of the methanol extract prepared above to 5 ml of reagent water for purging. This results in a 6,200 µg/kg concentration of each matrix spike compound when added to a 4 g sample (25,000 µg/kg for a 1 g sample).

12.2.3.3.2 Before performing an MS/MSD analysis, analyze the sample used for MS/MSD. If the sample analysis required dilution, the aliquots for the MS/MSD can be prepared at the same dilution as the least diluted analysis for which the sample results will be reported to the Agency. Sample dilutions must be performed in accordance with Section 10.1.7. Do **not** further dilute MS/MSD samples to get **either** spiked **or** non-spiked analytes within calibration range.

12.2.4 Calculations for MS/MSD

12.2.4.1 Calculate the concentrations of the matrix spike compounds using the same equations as used for target compounds (Section 11.2.1).

12.2.4.2 Calculate the recovery of each matrix spike compound using the following equation:

EQ. 14

$$Matrix\ Spike\ Recovery = \frac{SSR - SR}{SA} \times 100$$

Where,
SSR = Spiked sample result
SR = Sample result
SA = Spike added

12.2.4.3 Calculate the relative percent difference (RPD) of the recoveries of each compound in the matrix spike and matrix spike duplicate as follows:

EQ. 15

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

Where,
MSR = Matrix spike recovery
MSDR = Matrix spike duplicate recovery

The vertical bars in the formula above indicate the absolute value of the difference, hence the RPD is always expressed as a positive value.

12.2.5 Technical Acceptance Criteria for MS/MSD

12.2.5.1 All MS/MSDs must be analyzed on a GC/MS system meeting the GC/MS instrument performance check, initial calibration, initial calibration verification, and continuing calibration technical acceptance criteria defined in Sections 9.2.4, 9.3.5, 9.4.5 and 9.5.5, respectively.

12.2.5.2 The MS/MSDs must be analyzed or reanalyzed within the contract required holding time defined in Section 8.3.

12.2.5.3 All MS/MSDs must have associated method blanks, storage blanks, and instrument blanks meeting the blank technical acceptance criteria defined in Section 12.1.4.

12.2.5.4 The percent recovery of each of the system monitoring compounds in the MS/MSDs must be within the technical acceptance windows listed in Table 7.

12.2.5.5 The response for each of the internal standards in the MS/MSD must be within the inclusive range of -50.0 percent and +100.0 percent of the EICP area of the internal standards in the most recent continuing calibration analysis or 50 µg/L initial calibration standard, if appropriate.

12.2.5.6 The retention time shift for each of the internal standards in the MS/MSD must be within ± 0.50 minutes (30 seconds) between the MS/MSD internal standard retention times and the most recent continuing calibration standard (or 50 µg/L initial calibration standard) internal standard retention times.

12.2.5.7 The relative retention time (RRT) of the target compounds and system monitoring compounds in the MS/MSD must be within ±0.06

(RRT) units of its relative retention time in the continuing calibration standard or 50 µg/L initial calibration standard, if appropriate.

12.2.5.8 Excluding those ions in the solvent front, no ion from a target or non-target compound may saturate the detector. No target compound concentration may exceed the upper limit of the initial calibration range unless a diluted aliquot of the sample is also analyzed according to the procedures in Section 10.1.7.

12.2.5.9 The technical acceptance criteria for MS/MSD compound recoveries and RPD are given in Table 8. As these limits are only advisory, no further action by the laboratory is required. However, frequent failures to meet the limits for recovery or RPD warrant investigation by the laboratory, and may result in questions from the Agency.

12.2.6 Corrective Action for MS/MSD

Any MS/MSD that does not meet the technical acceptance criteria for MS/MSD must be reanalyzed at no additional cost to the Agency. Both sets of data must be reported.

12.2.6.1 Corrective actions for failure to meet GC/MS instrument performance check, initial and continuing calibration and initial calibration verification must be completed before the analysis of any QC samples.

12.2.6.2 Corrective actions for failure to meet blank technical acceptance criteria must be met before the analysis of any QC samples.

12.2.6.3 Corrective actions for system monitoring compound recoveries and/or internal standard compound responses defined in Section 11.4.4 must be completed before QC sample results are reported.

12.2.6.4 Corrective actions for system monitoring compound relative retention times and/or internal standard compound retention times defined in Section 11.4.5 must be completed before QC sample results are reported.

12.2.6.5 If the technical acceptance criteria for MS/MSD analysis are not met, the contractor shall determine whether the non-compliance is due to the sample matrix or GC/MS system problems.

12.2.6.6 If the non-compliance is found to be due to a sample matrix effect, take the following corrective action steps:

- Reanalyze the sample. EXCEPTION: If system monitoring compound recoveries or internal standard compound responses in a sample used for a matrix spike or matrix spike duplicate were outside the technical acceptance criteria, then it should be reanalyzed only if system monitoring compound recoveries and internal standard compound responses met acceptance criteria in both the matrix spike and matrix spike duplicate analyses.

- If the MS/MSD recoveries meet the technical acceptance criteria in the reanalyzed sample, then the problem was within the Contractor's control. The contractor should make every effort to reanalyze the sample within the contract required holding times. If the reanalysis was performed within holding times, then submit data only from the reanalysis. If the reanalysis was performed outside holding times, then submit both sets of data.

- If the MS/MSD recoveries fail to meet the acceptance criteria in the reanalysis, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables using the suffixes on Exhibit B.

12.3 SDG-Specific Performance Evaluation (PE) Samples

12.3.1 Summary of SDG-Specific PE Samples

The Region I Performance Evaluation (PE) program has two functions, (1) to evaluate laboratory operation and protocols over a period of time, and (2) to provide information on the quality of individual data packages.

12.3.2 Frequency of SDG-Specific PE Samples

12.3.2.1 The Region will submit PE samples with every SDG per parameter, matrix and concentration level (as available). The Region may obtain these SDG-Specific PE samples from either a commercial vendor or from the CLP National Program Office (NPO) which provides PE samples in support of the Superfund program. PE samples provided by the CLP-NPO are referred to as "EPA generated".

12.3.2.2 When the Region submits aqueous trip and/or equipment blanks and/or Performance Evaluation samples (PEs) with soil/sediment/solid field samples, then the Contractor shall not perform an MS/MSD analysis on the aqueous matrix (trip blank, equipment blank, PE sample). When the Region submits an aqueous PE sample with aqueous field samples, then the Contractor shall not choose the PE sample for MS/MSD analysis.

12.3.2.3 If the PE sample is received as an ampulated standard extract, the ampulated PE sample is not considered to be another matrix type.

12.3.3 Procedure for Preparing SDG-Specific PE Samples

12.3.3.1 Instructions for preparation of the PE samples will be included with each submission of PE samples.

12.3.3.2 If PE sample directions do not apply to a PE sample received, then the Contractor must contact the RSCC to ascertain whether or not to analyze the PE sample and to obtain appropriate PE sample directions.

12.3.4 Calculations for SDG-Specific PE Samples

12.3.4.1 For EPA-generated and commercially prepared PE samples that are submitted with each SDG, the Contractor must correctly identify and quantitate all TCL compounds using the criteria presented in Section 11.0 - Data Analysis and Calculations.

12.3.5 Technical Acceptance Criteria for SDG-Specific PE Samples

12.3.5.1 All SDG-Specific PE samples must be analyzed under the same GC/MS conditions set up in Section 9.0 and must meet the same technical acceptance criteria established for sample analysis defined in Section 11.3.

12.3.5.2 EPA-generated PE samples included with the SDG will be evaluated by the Region using a CLP NPO computer program called PeacTOOLs. PeacTOOLs rates the PE sample results based on statistically generated confidence intervals.

12.3.5.3 The results of commercially supplied PE samples will be evaluated using the vendors' statistically generated confidence intervals.

12.3.5.4 Contractor results for the SDG-Specific PE samples will be evaluated using the most recent Region I data validation criteria for PE samples.

12.3.5.5 At a minimum, the PE results will be evaluated for compound identification, quantitation, and sample contamination. Confidence intervals for the quantitation of target compounds are based on reported values using population statistics. The Agency may adjust the criteria on any given PE sample to compensate for unanticipated difficulties with a particular sample. Normally, a fraction of the compounds spiked into the sample are not specifically listed in the contract. Contractors must use the guidelines described in Section 11.1.2 for identification of non-

target compounds. Tentative identification of these non-target compounds is evaluated and integrated into the evaluation process.

12.3.6 Corrective Action for SDG-Specific PE Samples

12.3.6.1 The corrective actions for SDG Specific PE sample results which do not meet the technical acceptance criteria defined in Section 12.3.5.1 above are the same corrective actions outlined for sample analysis in Section 11.4.

12.3.6.2 If an SDG Specific PE sample evaluated by Region I as described in Sections 12.3.5.2 through 12.3.5.5 above, indicates unacceptable laboratory performance, then the Contractor may be required to reanalyze all samples, standards, blanks and QC samples associated with the unacceptable PE sample result (if sufficient volume remains) and/or analyze a new PE sample at no additional cost to the Agency. Unacceptable laboratory performance includes either a TCL false positive result, false negative result, and/or compound misquantitation (reported result exceeds $\pm$ 3 sigma of the spiked compound concentration).

12.3.6.3 SDG Specific sample results reported with unacceptable PE results shall be subject to a commensurate reduction in sample price or zero payment due to data rejection, depending upon the impact of the non-compliance on data usability.

12.4 CLP Quarterly Blind (QB) Laboratory Evaluation Program

12.4.1 Summary of CLP QB Samples

The Region will also submit quarterly laboratory evaluation samples for specified analyses in conjunction with the CLP Quarterly Blind (QB) program. The results from the analysis of these QB samples will be used by the Region to verify the Contractor's continuing ability to produce acceptable analytical data. The results will also be used to assess the precision and accuracy of the analytical methods for specific analytes.

12.4.2 Frequency of CLP QB Samples

12.4.2.1 The Region will submit laboratory evaluation samples on a quarterly basis for specified analyses in conjunction with the CLP Quarterly Blind (QB) program.

12.4.3 Procedure for Preparing CLP QB Samples

12.4.3.1 Instructions for preparation of the QB samples will be included with each submission of QB samples.

12.4.4 Calculations for CLP QB Samples

12.4.4.1 The Contractor must correctly identify and quantitate all TCL compounds using the criteria presented in Section 11.0 - Data Analysis and Calculations.

12.4.5 Technical Acceptance Criteria for CLP QB Samples

12.4.5.1 The QB samples must be analyzed under the same GC/MS conditions set up in Section 9.0 and must meet the same technical acceptance criteria established for sample analysis defined in Section 11.3.

12.4.5.2 The QB samples will be scored and the results will be used to assess the precision and accuracy of the analytical methods for specific analytes.

12.4.5.3 At a minimum, the results are evaluated for compound identification, quantitation, and sample contamination. Confidence intervals for the quantitation of target compounds are based on reported values using population statistics. The Agency may adjust the scores on any given laboratory evaluation sample to compensate for unanticipated difficulties with a particular sample. Normally, a fraction of the compounds spiked into the sample are not specifically listed in the contract. Contractors must use the guidelines described in Section 11.1.2 for

identification of non-target compounds. Tentative identification of these non-target compounds is evaluated and integrated into the evaluation process.

12.4.5.4 The Contractor's performance on the QB samples will be measured and reported as follows:

12.4.5.4.1 Acceptable, No Response Required (Score greater than or equal to 90%): Data meets most or all of the scoring criteria.

12.4.5.4.2 Acceptable, Response Explaining Deficiency(ies) Required (Score greater than or equal to 75% but less than 90%): Deficiencies exist in the Contractor's performance.

12.4.5.4.3 Unacceptable Performance (Score less than 75%): Deficiencies exist in the Contractor's performance to the extent that the Agency has determined that the Contractor has not demonstrated the capability to meet the contract requirements.

12.4.5.4.4 In the case of Sections 12.4.5.4.2 and 12.4.5.4.3 above, the Contractor shall respond to the deficiency(ies) and the action(s) taken to correct the deficiency(ies) in a letter to the Contract Officer and the Project Officer, within 14 days of receipt of notification from the Agency.

12.4.6 Corrective Action for CLP QB Samples

12.4.6.1 The corrective actions for QB sample results which do not meet the technical acceptance criteria defined in Section 12.4.5.1 above are the same corrective actions outlined for sample analysis in Section 11.4.

12.4.6.2 After receipt and review of the Contractor's deficiency letter (Section 12.4.5.4.4), the Project Officer or Contracting Officer will notify the Contractor concerning the remedy for their unacceptable performance. The Contractor may expect, but the Agency is not limited to, the following actions: commensurate reduction in sample price, zero payment due to data rejection, reduction of the number of samples sent under the contract, suspension of sample shipment to the Contractor, a GC/MS tape audit, a data package audit, an on-site laboratory evaluation, a remedial laboratory evaluation sample, and/or contract sanctions, such as a Cure Notice.

NOTE: The Contractor's prompt response demonstrating that corrective actions have been taken to ensure the Contractor's capability to meet contract requirements may facilitate continuation of sample scheduling.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When it is not feasible to reduce waste at the source, the Agency recommends recycling as the next best option.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable Federal, State and local rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions.

16.0 REFERENCES

16.1 USEPA, "Contract Laboratory Program, Statement of Work for Organic Analysis;" OLM03.1, PB95-963503, August, 1994.

16.2 USEPA, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,"SW846/8260A, Third Edition, September, 1994.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

BFB Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	8.0-40.0 percent of mass 95
75	30.0-66.0 percent of mass 95
95	base peak, 100 percent relative abundance
96	5.0-9.0 percent of mass 95 (see note)
173	less than 2.0 percent of mass 174
174	50.0-120.0 percent of mass 95
175	4.0-9.0 percent of mass 174
176	93.0-101.0 percent of mass 174
177	5.0-9.0 percent of mass 176

NOTE: All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120.0 percent that of m/z 95.

Table 2

Characteristic Ions for Volatile Target Compounds

Analyte	Primary Quantitation Ion	Secondary Ion(s)
Dichlorodifluoromethane	85	87
Chloromethane	50	52
Vinyl Chloride	62	64
Bromomethane	94	96
Chloroethane	64	66
Trichlorofluoromethane	101	103
1,1-Dichloroethene	96	61, 63
Acetone	43	58
Carbon Disulfide	76	78
Methylene chloride	84	49, 86
trans-1,2-Dichloroethene	96	61, 98
1,1-Dichloroethane	63	65, 83
2,2-Dichloropropane	77	97
2-Butanone	43*	57, 72
cis-1,2-Dichloroethene	96	61, 98
Chloroform	83	85
Bromochloromethane	128	49, 130
1,1,1-Trichloroethane	97	99, 61
1,1-Dichloropropene	75	110, 77
Carbon Tetrachloride	117	119
Benzene	78	77
1,2-Dichloroethane	62	98
Trichloroethene	95	130, 132
1,2-Dichloropropane	63	112
Bromodichloromethane	83	85, 127
Dibromomethane	93	95, 174
4-Methyl-2-Pentanone	43	58, 85
trans-1,3-Dichloropropene	75	110
Toluene	92	91
cis-1,3-Dichloropropene	75	110
1,1,2-Trichloroethane	83	97, 85
2-Hexanone	43	58
Tetrachloroethene	164	129, 166
1,4-Dioxane	88	58, 43
Tetrahydrofuran	71	72, 42
1,3-Dichloropropane	76	78

Table 2 (continued)

Analyte	Primary Quantitation Ion	Secondary Ion(s)
Dibromochloromethane	129	127
Bromoform	173	175, 252
Isopropylbenzene	105	120
1,2-Dibromoethane	107	109, 188
Chlorobenzene	112	77, 114
Ethylbenzene	91	106
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Xylenes	106	91
Styrene	104	78
Bromobenzene	156	77, 158
N-Propylbenzene	91	120
1,2,3-Trichloropropane	75	77
2-Chlorotoluene	91	126
1,3,5-Trimethylbenzene	105	120
4-Chlorotoluene	91	126
tert-Butylbenzene	119	91
1,2,4-Trimethylbenzene	105	120
sec-Butylbenzene	105	134
4-Isopropyltoluene	119	134, 91
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
N-Butylbenzene	91	134
1,2-Dichlorobenzene	146	111, 148
1,2-Dibromo-3-Chloropropane	75	155, 157
1,2,4-Trichlorobenzene	180	182
Hexachlorobutadiene	225	260
Naphthalene	128	--
1,2,3-Trichlorobenzene	180	182

* m/z 43 is used for quantitation of 2-Butanone, but m/z 72 **must** be present for positive identification.

Table 3

Volatile Internal Standards with Corresponding Target Compounds and System Monitoring Compounds Assigned for Quantitation

Fluorobenzene	Chlorobenzene-d_5
Dichlorodifluorobenzene	Dibromochloromethane
Chloromethane	Bromoform
Vinyl Chloride	Isopropylbenzene
Bromomethane	1,2-Dibromoethane
Chloroethane	Chlorobenzene
Trichlorofluoromethane	Ethylbenzene
1,1-Dichloroethene	1,1,1,2-Tetrachlorobenzene
Acetone	1,1,2,2-Tetrachlorobenzene
Carbon Disulfide	Xylenes
trans-1,2-Dichloroethene	Styrene
1,1-Dichloroethane	Bromobenzene
2,2-Dichloropropane	N-Propylbenzene
2-Butanone	1,2,3-Trichloropropane
cis-1,2-Dichloroethene	2-Chlorotoluene
Chloroform	1,3,5-Trimethylbenzene
Bromochloromethane	4-Chlorotoluene
1,1,1-Trichloroethane	tert-Butylbenzene
1,1-Dichloropropene	1,2,4-Trimethylbenzene
Carbon Tetrachloride	sec-Butylbenzene
Benzene	4-Isopropyltoluene
1,2-Dichloroethane	1,3-Dichlorobenzene
Trichloroethene	1,4-Dichlorobenzene
1,2-Dichloropropane	N-Butylbenzene
Bromodichloromethane	1,2-Dichlorobenzene
Dibromomethane	1,2-Dibromo-3-Chloropropane
4-Methyl-2-Pentanone	1,2,4-Trichlorobenzene
trans-1,3-Dichloropropene	Hexachlorobutadiene
Toluene	Naphthalene
cis-1,3-Dichloropropene	1,2,3-Trichlorobenzene
1,1,2-Trichloroethane	1,2-Dichlorobenzene-d4 (SMC)
2-Hexanone	4-Bromofluorobenzene (SMC)
Tetrachloroethene	
1,4-Dioxane	
Tetrahydrofuran	
1,3-Dichloropropane	
1,2-Dichloroethane-d4 (SMC)	

(SMC) = system monitoring compound

Table 4

Characteristic Ions for System Monitoring Compounds and Internal Standards for Volatile Organic Compounds with CAS Numbers

Compound	Primary Quantitation Ion	Secondary Ion(s)
SYSTEM MONITORING COMPOUNDS		
1,2-Dichloroethane-d4	65	67, 102
1,2-Dichlorobenzene-d4	152	115, 150
INTERNAL STANDARDS		
Fluorobenzene	96	77
Chlorobenzene-d_5	117	82, 119

Table 5

Relative Response Factor Criteria for Initial and Continuing Calibration of Volatile Organic Compounds

Volatile Compound	Minimum RRF	Maximum %RSD	Maximum %Diff
Dichlorodifluoromethane	0.050	≤30.0	±30.0
Chloromethane	0.050	≤30.0	±30.0
Vinyl Chloride	0.050	≤20.5	±25.0
Bromomethane	0.050	≤20.5	±25.0
Chloroethane	0.050	≤20.5	±25.0
Trichlorofluoromethane	0.050	≤20.5	±25.0
1,1-Dichloroethene	0.050	≤20.5	±25.0
Acetone	0.020	≤30.0	±30.0
Carbon Disulfide	0.050	≤30.0	±30.0
Methylene Chloride	0.050	≤30.0	±30.0
trans-1,2-Dichloroethene	0.050	≤20.0	±25.0
1,1-Dichloroethane	0.050	≤20.0	±25.0
2,2-Dichloropropane	0.050	≤20.0	±25.0
2-Butanone	0.020	≤30.0	±30.0
cis-1,2-Dichloroethene	0.050	≤20.0	±25.0
Chloroform	0.050	≤20.0	±25.0
Bromochloromethane	0.050	≤20.0	±25.0
1,1,1-Trichloroethane	0.050	≤20.0	±25.0
1,1-Dichloropropene	0.050	≤20.0	±25.0
Carbon Tetrachloride	0.050	≤20.0	±25.0
Benzene	0.050	≤20.0	±25.0
1,2-Dichloroethane	0.050	≤20.0	±25.0
Trichloroethene	0.050	≤20.0	±25.0
1,2-Dichloropropane	0.050	≤20.0	±25.0
Bromodichloromethane	0.050	≤20.0	±25.0
Dibromomethane	0.050	≤20.0	±25.0
4-Methyl-2-Pentanone	0.020	≤30.0	±30.0
trans-1,3-Dichloropropene	0.050	≤20.0	±25.0
Toluene	0.050	≤20.0	±25.0
cis-1,3-Dichloropropene	0.050	≤20.0	±25.0
1,1,2-Trichloroethane	0.050	≤20.0	±25.0
2-Hexanone	0.020	≤30.0	±30.0
Tetrachloroethene	0.050	≤20.0	±25.0
1,4-Dioxane	0.010	≤30.0	±30.0
Tetrahydrofuran	0.050	≤20.0	±25.0
1,3-Dichloropropane	0.050	≤20.0	±25.0

Table 5 (continued)

Volatile Compound	Minimum RRF	Maximum %RSD	Maximum %Diff
Dibromochloromethane	0.050	≤20.0	±25.0
Bromoform	0.050	≤20.0	±25.0
Isopropylbenzene	0.050	≤20.0	±25.0
1,2-Dibromoethane	0.050	≤20.0	±25.0
Chlorobenzene	0.050	≤20.0	±25.0
Ethylbenzene	0.050	≤20.0	±25.0
1,1,1,2-Tetrachloroethane	0.050	≤20.0	±25.0
1,1,2,2-Tetrachloroethane	0.050	≤20.0	±25.0
Xylenes	0.050	≤20.0	±25.0
Styrene	0.050	≤20.0	±25.0
Bromobenzene	0.050	≤20.0	±25.0
N-Propylbenzene	0.050	≤20.0	±25.0
1,2,3-Trichloropropane	0.050	≤20.0	±25.0
2-Chlorotoluene	0.050	≤20.0	±25.0
1,3,5-Trimethylbenzene	0.050	≤20.0	±25.0
4-Chlorotoluene	0.050	≤20.0	±25.0
tert-Butylbenzene	0.050	≤20.0	±25.0
1,2,4-Trimethylbenzene	0.050	≤20.0	±25.0
sec-Butylbenzene	0.050	≤20.0	±25.0
4-Isopropyltoluene	0.050	≤20.0	±25.0
1,3-Dichlorobenzene	0.050	≤20.0	±25.0
1,4-Dichlorobenzene	0.050	≤20.0	±25.0
N-Butylbenzene	0.050	≤20.0	±25.0
1,2-Dichlorobenzene	0.050	≤20.0	±25.0
1,2-Dibromo-3-Chloropropane	0.020	≤20.0	±25.0
1,2,4-Trichlorobenzene	0.050	≤20.0	±25.0
Hexachlorobutadiene	0.050	≤20.0	±25.0
Naphthalene	0.050	≤20.0	±25.0
1,2,3-Trichlorobenzene	0.050	≤20.0	±25.0
SYSTEM MONITORING COMPOUNDS			
1,2-Dichlorobenzene-d4	0.010	≤30.0	±30.0
1,2-Dichloroethane-d4	0.010	≤30.0	±30.0

Table 6

The "X" Factor Table

X Factor	Estimated Concentration Range[1] (µg/kg)	Take This Volume of Methanol Extract[2] (µl)
0.25 - 5.0	500 - 10,000	100
0.5 - 10.0	1000 - 20,000	50
2.5 - 50.0	5000 - 100,000	10
12.5 - 250	25,000 - 500,000	100 of 1/50 dilution[3]

Calculate appropriate dilution factor for concentrations exceeding those in the table.

[1] Actual concentration ranges could be 10 to 20 times higher than this if the compounds are halogenated and the estimates are from GC/FID.

[2] The volume of methanol added to the 5 ml of water being purged should be kept constant. Therefore, add to the 5 ml syringe whatever volume of methanol is necessary to maintain a volume of 100 µl added to the syringe.

[3] Dilute an aliquot of the methanol extract and then take 100 µl for analysis.

Table 7

System Monitoring Compound Recovery Limits

Compound	% Recovery All Matrices
1,2-Dichloroethane-d4	80-120
1,2-Dichlorobenzene-d4	80-120

Table 8

Matrix Spike Recovery and
Relative Percent Difference Limits

Compound	% Recovery All Matrices	RPD All Matrices
Vinyl Chloride	80-120	25
Trichloroethene	80-120	25
1,2-Dichloroethane	80-120	25
Carbon Tetrachloride	80-120	25
Benzene	80-120	25
1,2-Dichloropropane	80-120	25
Bromoform	80-120	25
1,1,2-Trichloroethane	80-120	25
cis-1,3-Dichloropropene	80-120	25
Tetrachloroethene	80-120	25
1,2-Dibromomethane	80-120	25
1,4-Dichlorobenzene	80-120	25
2-Hexanone	80-120	25
Tetrahydrofuran	80-120	25

APPENDIX A - SCREENING OF HEXADECANE EXTRACTS FOR VOLATILES

1.0 SCOPE AND APPLICATION

1.1 The hexadecane extraction and screening methods for purgeables described in this section are designed to aid the analyst in deciding whether a soil sample is low or medium level in order to prevent saturation of the purge and trap system and/or the GC/MS system. These or other screening methods should be used, particularly if there is some doubt about the level of organics in a sample. This is especially true in soil/sediment analysis. Water samples may also be screened to determine an appropriate dilution factor for analysis.

1.2 These extractions and preparation procedures were developed for rapid screening of water and soil/sediment samples from hazardous waste sites. The design of the methods thus does not stress efficient recoveries or low limits of quantitation. Rather, the procedures were designed to screen at moderate recovery and sufficient sensitivity for a broad spectrum of organic chemicals. The results of the analyses thus may reflect only a minimum of the amount actually present in some samples. This is especially true if water soluble solvents are present.

2.0 SUMMARY OF METHODS

2.1 Sample Preparation

2.1.1 Water

A 40 ml aliquot of sample is extracted with 2 ml of hexadecane. This provides a minimum quantitation limit (MQL) as follows:

Compounds	MQL (µg/L)
non-halogenated aromatics	40-50
halogenated methanes	80-1000
halogenated ethanes	400-500

2.1.2 Soil/Sediment

40 ml of reagent water are added to 10 g (wet weight) of soil/sediment and shaken. The water phase is in turn extracted with 2 ml of hexadecane. This provides a minimum quantitation limit of approximately four times higher than those listed for water.

2.2 GC/FID Screening

The hexadecane extracts of water and soil/sediment are screened on a gas chromatograph/flame ionization detector (GC/FID). The results of the screen will determine if volatile organics are to be analyzed by low or medium level GC/MS procedures if the sample is a soil/sediment, or to determine the appropriate dilution factor if the sample is water. Note: The flame ionization detector varies considerably in sensitivity when comparing aromatics and halogenated methanes and ethanes. Halomethanes are approximately 20x less sensitive than aromatics and haloethanes are approximately 10x less sensitive than aromatics. Low molecular weight, water soluble solvents (e.g., alcohols and ketones, will not be extracted from the water, and therefore will not be detected by the GC/FID.

3.0 INTERFERENCES

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.0 SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined, however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should be made available to all personnel involved in these analyses. Use all reagents in fume hoods whenever possible. Always wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing when working with these reagents.

5.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this SOW is the responsibility of the Contractor.

5.1 Glassware

5.1.1 Syringes - 0.5 ml

5.1.2 Vials and Caps - 2 ml capacity for GC autosampler

5.1.3 Pasteur Pipets - disposable

5.1.4 Centrifuge Tube - 50 ml with ground glass stopper or Teflon-lined screw cap.

5.1.5 Volumetric Flask - 50 ml with ground glass stopper.

5.2 Balance - analytical, capable of accurately weighing ±0.0001 g.

5.3 Pyrex Glass Wool

5.4 Balances - analytical, capable of accurately weighing ±0.0001 g, and a top-loading balance capable of weighing 100 g ±0.01 g. The balances must be calibrated with class S weights or known reference weights once per each 12-hour work shift. The balances must be calibrated with class S weights at a minimum of once per month. The balances must also be annually checked by a certified technician.

5.5 Centrifuge

5.6 Gas Chromatograph/Flame Ionization Detector (GC/FID) System

5.6.1 Gas Chromatograph (GC) - an analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.2 Gas Chromatography Column - 30 m (or longer) x 2 mm ID glass column packed with 10% OV-101 on 100-120 mesh chromosorb W-HP (or equivalent). The column temperature should be programmed from 80 °C to 280 °C at 16 C°/min. and held at 280 °C for 10 minutes.

5.6.3 Flame Ionization Detector (FID)

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Reagent Water - defined as water in which an interferent is not observed at the CRQL of each analyte of interest.

6.1.2 Hexadecane and Methanol - pesticide residue analysis grade or equivalent.

6.2 Standards

6.2.1 Introduction

The Contractor must provide all standard solutions to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the contractor and presented upon request.

6.2.2 Stock Standard Solutions

6.2.2.1 Stock standard solutions (1 µg/µl) can be prepared from pure standard materials or purchased as certified solutions.

6.2.2.2 Prepare stock standard solutions by accurately weighing about 0.01 g of pure material. Dissolve the material in methanol and dilute to volume in a 10 ml volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 97% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

6.2.3 Working Standard Solutions

6.2.3.1 Standard Mixture #1

Prepare a working standard mixture containing benzene, toluene, ethylbenzene and xylene at 100 ng/µl of each compound in methanol.

6.2.3.2 Standard Mixture #2

Prepare a working standard mixture containing n-nonane and n-dodecane at 100 ng/µl of each compound in methanol.

6.2.4 Storage of Standards

Transfer all standard solutions into multiple Teflon-sealed screw-cap vials. Store, with no head-space, at -10 °C to -20 °C, and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. These solutions must be replaced after six months, or sooner, if comparison with quality control check samples indicates a problem. Standards prepared from gases or reactive compounds such as styrene must be replaced after two months, or sooner, if comparison with quality control check samples indicates a problem.

7.0 QUALITY CONTROL

7.1 Method Blank

7.1.1 Summary

A method blank is a volume of clean reagent water taken through the extraction and screening procedure. The volume of reagent water used must be approximately equal to the volume of associated samples. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

7.1.2 Frequency

One method blank must be extracted and analyzed on each GC/FID system used to screen samples for the following, whichever is most frequent.

- Each SDG, or
- Each 20 samples in a SDG, including matrix spike and matrix spike duplicate, or
- When samples are extracted.

7.1.3 Procedure

For screening of volatile organics, a method blank consists of a 40 ml volume of reagent water extracted with 2 ml of hexadecane. The hexadecane extract is then screened on a GC/FID system.

8.0 CALIBRATION AND STANDARDIZATION

8.1 GC/FID Operating Conditions

Refer to Section 5.5.2 for recommended column temperature program.

8.2 GC Calibration

8.2.1 Summary

Prior to sample analysis each GC/FID system must be standardized for half scale response.

8.2.2 Frequency

Each GC/FID system must be calibrated at the beginning of each 12-hour shift.

8.2.3 Procedure

8.2.3.1 Add 200 µl of each of working standard mixtures #1 and #2 (Section 6.2.3) to separate 40 ml portions of reagent water in 50 ml volumetric flasks. Immediately add 2 ml of hexadecane, cap the flask, and shake vigorously for 1 minute. Let phases separate. Open the flask and add sufficient reagent water to bring the hexadecane layer into the neck of the flask. Transfer approximately 1 ml of the hexadecane layer to a 2 ml GC vial.

8.2.3.2 Inject 1-2 µl of the extracts that contain approximately 10 ng/µl each of standard mixture #1 and standard mixture #2 compounds.

9.0 PROCEDURE

9.1 Sample Preparation

9.1.1 Water

9.1.1.1 Allow the contents of the 40 ml sample vial to come to room temperature. Quickly transfer the contents of the 40 ml sample vial to a 50 ml volumetric flask. Immediately add 2 ml of hexadecane, cap the flask, and shake vigorously for 1 minute. Let phases separate. Open the flask and add sufficient reagent water to bring the hexadecane layer into the neck of the flask.

9.1.1.2 Transfer approximately 1 ml of the hexadecane layer to a 2 ml GC vial. If an emulsion is present after shaking the sample, break it by doing the following:

- Pulling the emulsion through a small plug of Pyrex glass wool packed in a pipet, or
- Transferring the emulsion to a centrifuge tube and centrifuging for several minutes.

9.1.2 Soil/Sediment

Add approximately 10 g of soil/sediment (wet weight) to 40 ml of reagent water in a 50 ml centrifuge tube with a ground glass stopper or Teflon-lined cap. Cap and shake vigorously for 1 minute. Centrifuge the capped flask briefly. Quickly transfer supernatant water to a 50 ml volumetric flask equipped with a ground-glass stopper. Follow 9.1.1 starting with the addition of 2 ml of hexadecane.

9.2 GC/FID Analysis

Inject the same volume of sample hexadecane extract as the extracted standard mixture in 8.2.3.

9.2.1 GC/FID Chromatogram Interpretation -- Following are two options for interpreting the GC/FID Chromatograms.

9.2.1.1 Option A is to use standard mixture #1 containing the aromatics to calculate an approximate concentration of the aromatics in the sample. Use this information to determine the proper dilution for purge and trap if the sample is water, or whether to use the low or medium level GC/MS purge and trap methods if the sample is soil/sediment (see Table 1, Section 9.3 for guidance). This should be the best approach; however, the aromatics may be absent or obscured by higher concentrations of other purgeables. In these cases, Option B may be the best approach.

9.2.1.2 Option B is to use standard mixture #2 containing n-nonane and n-dodecane to calculate a factor. Use the factor to calculate a dilution for purge and trap of a water sample or to determine whether to use the low or medium level GC/MS purge and trap methods for soil/sediment samples (see Table 1, Section 9.3 for guidance). All purgeables of interest have retention times less than the n-dodecane.

9.3 Analytical Decision Point

9.3.1 Water

9.3.1.1 Compare the chromatograms of the hexadecane extract of the sample with those of the reagent blank and extract of the standard.

9.3.1.2 If no peaks are noted, other than those also in the reagent blank, analyze a 5 ml water sample by purge and trap GC/MS.

9.3.1.3 If peaks are present prior to the n-dodecane and the aromatics are distinguishable, follow Option A (Section 9.2.1).

9.3.1.4 If peaks are present prior to the n-dodecane but the aromatics are absent or indistinguishable, use option B as follows: if all peaks are ≤3% of the n-nonane, analyze a 5 ml water sample by purge and trap GC/MS. If any peaks are ≥3% of the n-nonane, measure the peak height or area of the major peak and calculate the dilution factor as follows:

$$\frac{\text{Peak area of sample major peak}}{\text{Peak area of n-nonane}} \times 50 = \text{dilution factor}$$

The water sample will be diluted using the calculated factor just prior to purge and trap GC/MS analysis.

9.3.2 Soil/Sediment

9.3.2.1 Compare the chromatograms of the hexadecane extract of the sample with those of the reagent blank and extract of the standard.

9.3.2.2 If no peaks are noted, other than those also in the reagent blank, analyze a 5 g sample by low level GC/MS.

9.3.2.3 If peaks are present prior to the n-dodecane and the aromatics are distinguishable, follow Option A (Section 9.2.1) and the concentration information in Table 1, to determine whether to analyze by low or medium level method.

9.3.2.4 If peaks are present prior to the n-nonane but the aromatics are absent or indistinguishable, and using Option B as follows, calculate a factor using the following formula:

$$\frac{\text{Peak area of sample major peak}}{\text{Peak area of n-nonane}} = \text{X Factor}$$

Table 1
Determination of GC/MS Purge and Trap Method

X Factor	Analyze by	Approximate Concentration Range* (µg/Kg)
0-1.0	low level method	0-1,200
> 1.0	medium level method	>1,200

* This concentration range is based on the response of aromatics to GC/FID. When comparing GC/FID responses, the concentration for halomethanes is 20 times higher, and that for haloethanes is 10 times higher.

APPENDIX B - MODIFIED SW-846 METHOD 5035 FOR VOLATILES IN LOW LEVEL SOILS

1.0 SCOPE AND APPLICATION

1.1 The analytical method that follows is designed to analyze low level sediment and soil samples from hazardous waste sites for the volatile organic compounds on the Target Compound List (TCL, see Exhibit C). The method includes sample preparation, screening to determine the approximate concentration of organic constituents in the sample, and the actual analysis which is based on a closed-system purge and trap gas chromatograph/mass spectrometer (GC/MS) method.

2.0 SUMMARY OF METHOD

2.1 Low level volatile organic compounds are determined by analyzing approximately 5 g of sample, in a pre-weighed vial with a septum-sealed screw-cap (see Section 5.0) that already contains a stirring bar and a sodium bisulfate preservative solution. Note: The sodium bisulfate preservative and the stirring bar may be omitted under certain circumstances (see Sections 9.3.2 and 9.3.8). The entire vial is placed into the instrument carousel. Immediately before analysis, organic-free reagent water, surrogates, and internal standards are automatically added without opening the sample vial. The vial containing the sample is heated to 40°C and the volatiles purged through a sorbent trap using an inert gas combined with agitation of the sample. When purging is complete, the trap is heated and backflushed with helium to desorb the purgeable compounds onto a gas chromatograph column. The gas chromatograph is temperature-programmed to separate the purgeable compounds which are then detected with a mass spectrometer.

2.2 The sample introduction technique in Section 2.1 is not applicable to all samples. If sample screening indicates that the soil/sediment sample should be analyzed as a medium level sample, the Contractor shall follow the procedure described in Exhibit D-VOA Section 10.1.5 for medium level soil/sediment samples.

3.0 INTERFERENCES

3.1 Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks as described in Exhibit D-VOA Section 12. The use of non-Polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during storage and handling.

3.3 Contamination by carryover can occur whenever medium level and low level samples are sequentially analyzed. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device. The trap and other parts of the system are also subjected to contamination; therefore, frequent bakeout and purging of the entire system may be required.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4.0 SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

4.2 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/Mass approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this SOW is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the SDG Narrative.

5.1 Sample Containers

The specific sample containers required will depend on the purge-and-trap system to be employed. Several systems are commercially available. Some systems employ 40-mL clear vials with a special frit and equipped with two PTFE-faced silicone septa. Other systems permit the use of any good quality glass vial that is large enough to contain at least 5 g of soil or solid material and at least 10 mL of water, and that can be sealed with a screw-cap containing a PTFE-faced silicone septum. The Contractor shall consult the purge-and-trap system manufacturer's instructions regarding the suitable specific vials, septa, caps, and mechanical agitation devices.

5.2 Glassware

5.2.1 Syringes - 25 mL glass hypodermic syringes with Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used). 5.0, 1.0, and 0.5 mL syringes gas-tight with shut-off valve.

5.2.2 Syringe valve - 2-way with Luer ends.

5.2.3 Micro syringes - 25 μL with a 2 inch x 0.006 inch ID, 22° bevel needle (Hamilton #702N or equivalent). 10 and 100 μL.

5.2.4 60-mL, septum-sealed glass vials to collect samples for screening, dry weight determination.

5.2.5 40-mL, screw-cap, PTFE lined, septum-sealed glass vials. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

5.2.6 Volumetric flasks - Class A, 10-mL and 100-mL, with ground glass stoppers.

5.2.7 Disposable Pasteur pipettes.

5.3 Magnetic stirring bars - PTFE- or glass-coated, of the appropriate size to fit the sample vials. Consult manufacturer's recommendation for specific stirring bars. Stirring bars may be reused, provided that they are thoroughly cleaned between uses. The cleanliness must be certified with stirring bar blank analysis per batch of stirring bars cleaned at the same time. The data must be kept on record by the laboratory and provided upon EPA request. Consult the manufacturers of the purging device and the stirring bars for suggested cleaning procedures.

5.4 Balances - analytical, capable of accurately weighing ± 0.0001 g, and a top-loading balance capable of weighing 100 g ± 0.01 g. The balances must be calibrated with class S weights or known reference weights once per each 12-hour work shift. The balances must be calibrated with class S weights at a minimum of once per month. The balances must also be annually checked by a certified technician.

5.5 Purge and Trap Device - consists of a unit that automatically adds water, SMCs, and internal standards to a hermetically sealed vial containing the sample, purges the volatile compounds using an inert gas stream while agitating the contents of the vial, and also traps the released volatile compounds for subsequent desorption into the gas chromatograph. Such systems are commercially available from several sources and shall meet the following specifications.

5.5.1 The purging device should be capable of accepting a vial sufficiently large to contain a 5 g soil/sediment sample plus a magnetic stirring bar and 10 mL of water. The device must be capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 5 mL of organic-free reagent water into the sample vial while trapping the displaced headspace vapors. It must also be capable of agitating the sealed sample during purging, (e.g., using a magnetic stirring bar, sonication, or other means). The analytes being purged must be quantitatively transferred to an absorber trap. The trap must be capable of transferring the absorbed volatile compounds to the gas chromatograph.

5.5.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch. Starting from the inlet, the trap must contain equal amounts of the absorbents listed below. It is recommended that 1.0 cm of methyl silicone-coated packing (35/60) mesh (Davison, grade 15 or equivalent) be inserted at the inlet to extend the life of the trap.

- 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent)
- Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent
- Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen

Trapping materials other than those listed above may also be used, provided that they meet the specifications listed in Exhibit D-VOA Sections 6.4.2 and 6.4.4.

5.5.3 The desorber for the trap must be capable of rapidly heating the trap to 180°C. The polymer section of the trap should not be heated higher than 180°C and the remaining sections should not exceed 220°C during bakeout mode.

5.6 Gas Chromatograph/Mass Spectrometer (GC/MS) System

5.6.1 Gas chromatograph/mass spectrometer system specifications and requirements are described in Exhibit D-VOA Section 6.6.

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Reagent water - defined as water in which an interferant is not observed at or above the CRQL of the analytes of interest. Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g (1 lb) of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

6.1.1.1 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

6.1.1.2 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90 °C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

6.1.2 Methanol - pesticide quality or equivalent.

6.1.3 Sodium bisulfate - ACS reagent grade or equivalent.

6.2 Standards

6.2.1 The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

6.2.2 The Contractor shall follow the procedures described in Exhibit D-VOA Section 7.2 for preparing stock standards, secondary dilutions, and all working standard solutions.

6.3 Storage of Standard Solutions

6.3.1 The Contractor shall follow the procedures described in Exhibit D-VOA Section 7.3 for storage of all standard solutions.

6.3.2 The Contractor is responsible for maintaining the integrity of standard solutions and verifying prior to use. This means that standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in the solution.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Sample Collection and Preservation

7.1.1 Soil/sediment samples should be collected in field core sampling/storage containers (i.e., EnCore™ or equivalent) and 60 mL septum-sealed glass vials in sufficient quantity to perform the analysis. The field core sampling/storage containers should contain approximately 5 g of sample each. The Contractor shall transfer the contents of each field core sampling container immediately upon receipt into a closed-system sample vial prepared as described in Section 9.3 below. Record the date and time of transfer in a laboratory logbook. Also record the sample visual description including the color, approximate particle size and/or sample consistency in a laboratory logbook. The laboratory must prepare two samples in aqueous/sodium bisulfate, one sample in methanol, and the vial is for the determination of percent moisture. If soil/sediment samples are received in pre-prepared closed-system purge-and-trap sample vials as described in Section 9.3, then the Contractor shall proceed to Section 9.3.9 and determine final sample weight.

7.1.2 For soil samples collected in Encore™ samplers or equivalent the samples must be transferred to glass vials within 48 hrs of sample collection .

7.1.2 All samples must be iced or refrigerated at 4 °C (±2 °C) from the time of collection until analysis.

7.2 Procedure for Sample Storage

7.2.1 The samples must be protected from light and refrigerated at 4 °C (±2 °C) from the time of receipt until 60 days after delivery of a reconciled, complete sample data package to the Agency. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

7.2.2 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants and in a refrigerator used only for storage of volatile samples.

7.2.3 All volatile samples in an SDG must be stored together in the same refrigerator.

7.2.4 Storage blanks shall be stored with samples until all samples are analyzed.

7.2.5 Samples, sample extracts, and standards must be stored separately.

7.2.6 Volatile standards must be stored separately from semivolatile and pesticide/Aroclor standards.

7.3 Contract Required Holding Times

Analysis of soil/sediment samples must be completed within 10 days of Validated Time of Sample Receipt (VTSR). As part of the Agency's QA program, the Agency may provide Performance Evaluation (PE) samples as standard extracts which the Contractor is required to prepare per the instructions provided by the Agency. PE samples must be prepared and analyzed concurrently with the samples in the SDG. The contract required 10 day holding time does not apply to PE samples received as standard extracts.

7.3.1 For soil samples collected in Encore™ samplers or equivalent the samples must be transferred to glass vials within 48 hrs of sample collection . The date and time of transfer must be recorded in a laboratory logbook and submitted with the data package. A visual description including the color, approximate size of particles and/or sample consistency must be recorded in a laboratory logbook.

8.0 CALIBRATION AND STANDARDIZATION

8.1 Purge and Trap

8.1.1 Assemble a purge-and-trap device that meets the specification in Section 5.5 and that is connected to a gas chromatograph/mass spectrometer system.

8.1.2 Before initial use, condition the trap overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min, or according to the manufacturer’s recommendations. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, condition the trap for 10 min at 180°C while backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

8.1.3 Establish the purge-and-trap instrument operating conditions. Adjust the instrument to inject 5 mL of reagent water, to heat the sample to 40°C, and to hold the sample at 40°C for 1.5 minutes before commencing the purge process, or as recommended by the instrument manufacturer. Once established, the same purge and trap conditions must be used for the analysis of all standards, samples, and blanks.

8.2 Gas Chromatograph/Mass Spectrometer

The Contractor shall follow the instrument conditions described in Exhibit D-VOA Sections 9.1.2 and 9.1.3.

8.3 GC/MS Calibration (Tuning) and Ion Abundance

The Contractor shall follow the procedure described in Exhibit D-VOA Section 9.2. All technical acceptance criteria for the GC/MS performance check shall be met before any standards or samples, including MS/MSDs or required blanks, are analyzed. Any samples or required blanks analyzed when tuning technical acceptance criteria have

not been met will require reanalysis at no additional cost to the Agency.

8.4 Initial Calibration

The Contractor shall follow the procedure described in Exhibit D-VOA Section 9.3. However, the volume of reagent water used for calibration must be the same volume used for sample analysis (normally 5 mL added to the vial before sample addition plus the reagent water added by the instrument). The calibration standards should also contain approximately the same amount of the sodium bisulfate preservative as the sample (e.g., approximately 1 g), as the presence of the preservative will affect the purging efficiencies of the analytes. The internal standard solution must be added automatically, by the instrument, in the same fashion as used for the samples. Place the soil vial containing the solution in the instrument carousel. In order to calibrate the system monitoring compounds (SMCs) using standards at five concentrations, it may be necessary to disable the automatic addition of SMCs to each vial containing a calibration standard (consult the manufacturer's instructions). Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as recommended by the manufacturer.

All technical acceptance criteria for GC/MS initial calibration specified in Exhibit D-VOA Section 9.3.5 shall be met prior to the analysis of any samples, including MS/MSDs or required blanks. Any samples or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to the Agency.

8.5 Continuing Calibration

The Contractor shall follow the procedure for continuing calibration described in Exhibit D-VOA Section 9.4. However, the continuing calibration standard shall be prepared in the same manner as the initial calibration standard of the same concentration as specified in Section 8.4 above (i.e., addition of the sodium bisulfate preservative).

All technical acceptance criteria for continuing calibration specified in Exhibit D-VOA Section 9.4.5 shall be met prior to the analysis of any samples, including MS/MSDs or required blanks. Any samples or required blanks analyzed when continuing calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to the Agency.

9.0 PROCEDURE

9.1 The Contractor must determine whether a soil/sediment sample should be analyzed by the low or medium method. Samples may contain higher than expected quantities of purgeable organics that will contaminate the purge-and-trap system thereby requiring extensive cleanup and instrument maintenance. The Contractor may follow one of the screening procedures identified in Exhibit D-VOA Section 10.1.4.2. The screening data are used to determine which is the appropriate sample preparation procedure for the particular sample. If, based on the screening results, medium level analysis is required, the Contractor shall follow the procedure in Exhibit D-VOA Section 10.1.5. If the Contractor received a pre-weighed sample preserved in methanol (see Section 7.1.1), this sample shall be utilized for the medium level analysis. It is the responsibility of the Contractor to analyze the sample at the correct level.

9.2 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Regional Sample Control Coordinator to address the problem. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis.

9.3 Sample Preparation

9.3.1 The following steps apply to soil samples received in Encore™ samplers and the preparation of vials used for the analysis of low level soil/sediment samples by the closed-system purge-and-trap equipment described in this method.

If soils are received in vials then sample preparation begins at 9.3.9

9.3.2 Add a clean magnetic stirring bar to each clean vial. If the purge-and-trap device employs a means of stirring the sample other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stir bar is omitted.

9.3.3 Add approximately 1 g of sodium bisulfate preservative to each vial. If samples significantly smaller or larger than 5 g are to be used, adjust the amount of preservative added to correspond to approximately 0.2 g of preservative for each 1 g of sample. Enough sodium bisulfate should be present to ensure a sample pH of $\leq$2.

9.3.4 Add 5 mL of reagent water to each vial. The water and the preservative will form an acid solution that will reduce or eliminate the majority of the biological activity in the sample, thereby preventing biodegradation of the volatile target compounds.

9.3.5 Seal the vial with the screw-cap and septum seal. If the double-ended, fritted vials are used, seal both ends as recommended by the manufacturer.

9.3.6 Affix a label to each vial and weigh the prepared vial to the nearest 0.01 g. Record the tare weight.

9.3.7 Because volatile organics will partition into the headspace of the vial from the aqueous solution and will be lost when the vial is opened, system monitoring compounds, matrix spikes and internal standards should only be added to the vials after the sample has been added to the vial. The standards should be introduced either manually by puncturing the septum with a small-gauge needle or automatically by the purge-and-trap system just prior to analysis.

9.3.8 Using the Extrusion tool, open the sample collection device and transfer the contents (approximately 5 g) into the sample vial containing the preservative solution. This sample transfer must be performed rapidly to minimize loss of volatile compounds. Quickly brush any soil off the vial and immediately seal the vial with the septum and screw-cap. The soil vial is hermetically sealed and must remain so in order to guarantee the integrity of the sample. Gloves must be worn when handling the sample vial

since the vial has been tared. Record the date and time of sample transfer onto the pre-prepared vials and submit with the data package.

NOTE: Soil samples that contain carbonate minerals may effervesce upon contact with the acidic preservative solution in the sample vial. Therefore, if samples are known or suspected to contain high levels of carbonates, a test sample (from the 60 mL glass vial) should be added to a clean vial and checked for effervescence. If a rapid or vigorous reaction occurs, the Contractor may discard the test sample and proceed with sample preparation by transferring the contents of the field core sampling/storage container into a clean vial that does not contain the preservative.

9.3.9 Weigh the vial and contents to the nearest 0.01 g and record this weight. Sample weight is determined by subtracting the sample vial tared weight determined above from this final weight. Record the weights in a laboratory notebook. Report the weights in the data package. Report all discrepancies to the Regional Sample Control Coordinator immediately.

9.4 Sample Purge-and-Trap

9.4.1 Prior to sample purge, all soil/sediment samples must be allowed to warm to ambient temperature. Shake the vial gently, to ensure that the contents move freely and that stirring will be effective. Place the sample vial in the instrument carousel according to the manufacturer's instruction.

9.4.2 Without disturbing the hermetic seal on the sample vial, add 5 mL of reagent water, 10 uL of the internal standard spiking solution (Exhibit D-VOA Section 7.2.4.3), and 10 uL of the system monitoring compound spiking solution (Exhibit D-VOA Section 7.2.4.1). **All samples, including MS and MSD, standards, and blanks, within an SDG must have the same amount of reagent water added. Do not increase/change the amount of system monitoring compound and internal standard solution added.** Prior to purging, heat the sample vial to 40 °C for 1.5 minutes, or as described by the manufacturer.

9.4.3 Purge the sample with helium or another inert gas at a flow rate of 20 to 40 mL/minute for 11 minutes while the sample is being agitated with the magnetic stirring bar or other mechanical means. The purged analytes are allowed to flow out of the vial through a glass-lined transfer line to a trap packed with suitable sorbent materials.

9.4.4 If a non-cryogenic interface is to be utilized, place the purge-and-trap system in the desorb mode after the 11-minute purge, and preheat the trap to 180 °C without a flow of desorption gas. Start the flow of desorption gas at 10 mL/minute for about four minutes. Begin the temperature program of the gas chromatograph and start data acquisition.

9.4.5 If a cryogenic interface is to be utilized, place the purge-and-trap system in the desorb mode after the 11-minute purge, making sure that the cryogenic interface is at -150 °C or lower, and rapidly heat the trap to 180 °C while backflushing with an inert gas at 4 mL/minute for about 5 minutes. At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250 °C. Begin the temperature program of the gas chromatograph and start the data acquisition.

9.4.6 After desorbing the sample for 4 to 5 minutes, recondition the trap by returning the purge-and-trap system to the purge mode. Maintain the trap temperature at 180 °C. After approximately 10 minutes, turn off the trap heater and halt the purge flow through the trap. When the trap is cool, the next sample can be analyzed.

9.5 Sample Dilutions

If the on column concentration of any target compound exceeds the initial calibration range from the analysis of 5 g sample, a medium

level analysis must be analyzed utilizing the procedure and methodology described in Exhibit D-VOA. Guidance in performing dilutions and exceptions to this requirement are given in Sections 10.1.6.2 through 10.1.6.10 of Exhibit D-VOA.

9.6 Percent Moisture Determination

Percent moisture must be determined prior to sample analysis. The Contractor shall follow the procedure described in Exhibit D-VOA Section 10.3 for determining percent moisture of samples.

10.0 DATA ANALYSIS AND CALCULATIONS

The Contractor shall perform qualitative and quantitative analysis for the target and non-target compounds following the procedures described in Exhibit D-VOA Section 11.0. All technical acceptance criteria for sample analysis described in Exhibit D-VOA Section 11.3 shall be met or the corrective action for sample analysis described in Section 11.4 of Exhibit D-VOA shall be followed.

11.0 QUALITY CONTROL

11.1 Blank Analyses

11.1.1 Summary -- There are three different types of blanks required by this method.

11.1.1.1 METHOD BLANK - a volume of purified solid matrix (prepared as described in Sections 9.3.2 through 9.3.5) and carried through the entire analytical procedure. The weight of the purified solid matrix must be approximately equal to the weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

11.1.1.2 STORAGE BLANK - upon receipt of the first samples in an SDG, two of the sample vials to be used for the closed-system purge-and-trap analysis (prepared as described in Sections 9.3.2 through 9.3.5) are filled with reagent water. The vials are stored with the samples in the SDG under the same conditions. After all samples in the SDG have been analyzed, the storage blank is analyzed. The storage blank indicates whether contamination may have occurred during storage of samples.

11.1.1.3 INSTRUMENT BLANK - a 5.0 mL aliquot of reagent water that is added to the sample vial (prepared as described in Sections 9.3.2 through 9.3.5) and carried through the entire analytical procedure. Instrument blanks are analyzed after a sample which contains a target compound exceeding the initial calibration range. The results from the instrument blank analysis indicate whether there is contamination from a previous sample.

11.1.2 Frequency of Blank Analyses

11.1.2.1 The method blank **must** be analyzed at least once during every 12-hour time period on each GC/MS system used for volatile analysis (see Section 9.2.2 of Exhibit D-VOA for the definition of the 12-hour time period).

11.1.2.2 The method blank **must** be analyzed after the continuing calibration and before any samples, including matrix spike/matrix spike duplicates, or storage blanks are analyzed. The method blank must be analyzed after the initial calibration sequence if samples are analyzed before the 12-hour period expires. A method blank must be analyzed in each 12-hour time period in which samples, including matrix spikes/matrix spike duplicates, and storage blanks are analyzed.

11.1.2.3 A minimum of one storage blank must be analyzed per SDG after all samples for that SDG have been analyzed.

11.1.2.4 The Contractor must demonstrate that there is no carryover from contaminated samples before data from subsequent analyses may be used. Samples may contain target compounds at levels exceeding the initial calibration range. An instrument blank must be analyzed after the sample that exceeds the calibration range (also in the same purge inlet if an autosampler is used) or a sample that meets the maximum contamination criteria in Section 11.3.8 of Exhibit D-VOA must be analyzed. For these purposes, if the instrument blank meets the technical acceptance criteria for blank analyses or the sample meets the maximum contamination criteria, the system is considered to be uncontaminated. If the instrument blank or sample does not meet the criteria (i.e., contaminated), the system must be decontaminated. Until an instrument blank meets the blank technical acceptance criteria or a sample meets the maximum contamination criteria in Section 11.3.8 of Exhibit D-VOA, any samples analyzed since the original contaminated sample will require reanalysis at no additional cost to the Agency.

NOTE: Only the instrument blank which demonstrates that there was no carryover from the previous sample or the instrument blank that demonstrates that the system is clean (Section 12.1.4 Exhibit D-VOA) needs to be reported. Instrument blanks analyzed during the instrument decontamination process which exceed the requirements listed in Exhibit D-VOA Section 12.1.4 do not need to be reported.

11.1.3 Procedure for Blank Analyses

11.1.3.1 Method blanks shall be analyzed in the same manner as the associated samples, following the procedure described in Section 9.4.

11.1.3.2 Storage/instrument blanks shall be analyzed in the same manner as the associated samples following the procedure outlined in section 9.4.

11.1.3.3 A storage blank may be analyzed and reported as a soil sample if the SDG contains only soil samples.

11.1.3.4 Identify and quantitate analytes according to Section 11.0 of Exhibit D-VOA.

11.1.4 Technical Acceptance Criteria for Blank Analyses

11.1.4.1 All technical acceptance criteria for blank analyses described in Exhibit D-VOA Section 12.1.4 shall be met or corrective action for blank analyses described in Exhibit D-VOA Section 12.1.5 shall be followed.

11.2 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

11.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix on the methods used for volatile analyses, the Agency has prescribed a mixture of volatile target compounds to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method.

11.2.2 Frequency of MS/MSD

11.2.2.1 A matrix spike and matrix spike duplicate must be performed for each group of samples of a similar matrix for the following, whichever is most frequent:

- Each SDG, or
- Each matrix within an SDG, or
- Each group of samples of a similar concentration level (soils only).

MS/MSD samples shall be analyzed unless otherwise specified on the Traffic Report (TR). If no MS/MSD samples are specified on the

TR, the Contractor shall contact SMO to confirm that MS/MSD analyses are not required.

11.2.2.2 As a part of the Agency's QA/QC program, water rinsate samples and/or field/trip blanks (field QC) may accompany soil/sediment samples that are delivered to a laboratory for analysis. The Contractor shall not perform MS/MSD analysis on any of the field QC samples.

11.2.2.3 If the EPA Region designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample, less than the required amount, remaining to perform an MS/MSD, then the Contractor shall choose another sample to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify the Region (through SMO) that insufficient sample was received and identify the EPA sample selected for the MS/MSD analysis. The rationale for the choice of a sample other than the one designated by the Region shall be documented in the SDG Narrative.

11.2.2.4 If there is insufficient sample remaining for any of the samples in an SDG to perform an MS/MSD, then the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the Region for instructions. The Region will either approve that no MS/MSD is required, or specify an alternative means of performing the MS/MSD analysis. SMO will notify the Contractor of the resolution. The Contractor shall document the decision in the SDG Narrative.

11.2.2.5 If it appears that the Region has requested MS/MSD analysis at a greater frequency than required by the contract, the Contractor shall contact SMO. SMO will contact the Region to determine which samples should have an MS/MSD performed on them. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative. If this procedure is not followed, the Contractor will not be paid for the MS/MSD analysis performed at a greater frequency than required by the contract.

11.2.2.6 When a Contractor receives **only** a Performance Evaluation (PE) sample(s), no MS/MSD shall be performed within that SDG.

11.2.2.7 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the MS/MSD when the Region did not designate samples to be used for this purpose.

11.2.3 Procedure for Preparing MS/MSD

11.2.3.1 To prepare a matrix spike and matrix spike duplicate for low level soil/sediment samples, follow the procedure outlined in Section 9.3. Add 10 µL of the matrix spike solution (Exhibit D-VOA Section 7.2.4.2) either manually by puncturing the septum with a small-gauge needle or automatically by the purge-and-trap system just prior to analysis. Analyze the matrix spike and matrix spike duplicate samples by the procedure described in Section 9.4. Do **not** further dilute MS/MSD samples to get **either** spiked **or** non-spiked analytes within calibration range.

11.2.4 Calculations for MS/MSD

The Contractor shall calculate the concentrations of the matrix spike compounds in the matrix spike and matrix spike duplicate samples using the same equation as used for target compounds (Equation 6) Exhibit D-VOA Section 11.2.1.3. The recovery of each matrix spike compound in the matrix spike and matrix spike duplicate samples and the relative percent difference (RPD) of the recoveries shall be calculated as specified in Exhibit D-VOA Section 12.2.4.

11.2.5 Technical Acceptance Criteria for MS/MSD

All technical acceptance criteria for MS/MSD specified in Exhibit D-VOA Section 12.2.5 must be met or corrective action for MS/MSD in Exhibit D-VOA Section 12.2.6 shall be followed.